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PLASTEC REPORT 32

THE WEATHERABILITY OF POLYOLEFINS

DEPARTMENT OF DEFENSE

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THE WEATHERABILITY OF POLYOLEFINS

Joan B. Titus

Plastics Technical Evaluation Center
Dover, New Jersey

March 1968

PLASTEC REPORT 32

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by

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March 1968

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ABSTRACT

The "Weatherability of Polyolefins" is the first of a series of reports on the weather resistance of non-reinforced plastics. It covers the effects of the weathering components on polyolefins; exposure testing methods; means of stabilization and the effects of pigments. In addition, a few examples of successful polyolefin outdoor applications are given.

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Marbon Chemical
Phillips Petroleum Company
Sinclair-Koppers Company

TRADE NAMES

For identification purposes the following are trade names of plastic and related materials appearing in this report. The mention of a particular commercial product neither constitutes an endorsement by Plastec, nor a voucher for the accuracy of a manufacturer's claim unless specifically noted:

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Akroflex C	E.I. duPont de Nemours & Co., Inc.
Albron 408	Aluminum Co. of America
Alkathene	Imperial Chemical Industries, Ltd.
AM-101	Ferro Chemical Corp.
Black Pearls 71	Cabot Corp.
Carbolac-1, 46	Cabot Carbon Ltd.
CI 729	Ferro Corp.
Columbian 999	Columbian International Ltd.
Cyasorb UV 314, 1084	American Cyanamid Co.
DBR	Dow Chemical Co.
DHPB	Eastman Chemical Products, Inc.
DYNH	Union Carbide Plastics Co.
DYNK	Union Carbide Plastics Co.
Eastman Inhibitor DOBP	Eastman Chemical Products, Inc.
Eastman Inhibitor OPS	Eastman Chemical Products, Inc.
Elfo 8	Cabot Corp.
HCB	Dow Chemical Co.
JZF	Naugatuck Chemical Div., U.S. Rubber Co.
Kosmos BB	United Carbon Corp.
Mapico Red 297	Columbia Carbon Co.
Marlex	Phillips Chemical Co.
Micronex Beads W-6	Columbian Carbon Co.
Micronex MPC	Columbian Carbon Co.
Monarch 74	Cabot Corp.
Monastral Blue BT 380-D	E.I. duPont de Nemours & Co. Inc.
Neo Spectra Mk II	Columbian International Ltd.
Neozone D	E.I. duPont de Nemours & Co. Inc.
Peerless Mk. II	Columbian International Ltd.
Philblack A	Phillips Chemical Co.
Raven 15	Columbian International Ltd.
Regal	Cabot Corp.
RMB	Eastman Chemical Products, Inc.
SALOL	Dow Chemical Co.
Santonox	Monsanto Co.
Santowhite	Monsanto Co.
Statex 160	Columbian Carbon Co.
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Super Dylan-5503 6530 6515 7006 7004C	Tennessee Eastman Chemical Co.
TBS	Dow Chemical Co.
Tenite 800	Eastman Chemical Products, Inc.
Thermax	Thermatomic Carbon
Tinuvin-P, 326, 327	Geigy Chemical Corp.
Ti Pure R-110	E.I. duPont de Nemours & Co., Inc.
Unitane 0-310	American Cyanamid Co.
UV 9, 287, 313, 314, 531	American Cyanamid Co.
UVINUL - 40, 400, 490, 539	General Aniline & Film Corp.
Vulcan 3, 6, 9, XXX	Cabot Corp.
Weather-Ometer	Atlas Electric Devices Co.
Witco 100	Witco Chemical Co., Inc.
Zetafin 30, 70	Dow Chemical Co.

INTRODUCTION

It has been estimated that approximately one quarter of the output of the plastics in this country (approximately 3.63 billion pounds in 1967) goes into products which are subjected to outdoor exposure. Therefore, acceptable weatherability of these materials is vital to the success or failure of items which, in many cases, are worth several times the cost of the plastic material involved.

In the military, weathering is of utmost importance since the end items must withstand the extremes of arctic, tropic, and space environments as well as wide temperature and humidity variations.

To aid in the distribution of information on the weatherability of various plastics, PLASTEC is preparing a series of reports. The first report, published in January 1966, was concerned with reinforced plastics. This report is the first of a series to cover the non-reinforced plastics field. Polyolefins have been covered first because (1) they have the highest volume poundage and (2) they are one of the materials most affected by weathering.

No attempt has been made to enter into the continuing controversy on weathering test methods - an area which could entail a report by itself. However, the various test methods with their advantages and disadvantages have been listed as general information in order to properly evaluate the data provided.

The reader is reminded that this report is not intended to be a handbook on the weatherability of specific polyolefins, but to provide general information on the weathering aspects of this plastic family. This limitation is necessary because of the general failure of the report literature to identify the polyolefin being tested by exact specifications or company designation. This problem is compounded by the inability to accurately correlate data from the various exposure testing methods even when the specific material is known.

SECTION I. SUMMARY

Polyolefins as a class of materials have poor inherent weatherability, but they can be greatly improved by the addition of appropriate additives such as antioxidants, ultraviolet stabilizers, pigments, and carbon black.

Oxidation at low temperatures is negligible except in the presence of ultraviolet light. The degradation of polyethylene by ultraviolet radiation is caused by carbonyl groups derived from the initiator or generated during polymerization and must be controlled by ultraviolet absorbers, antioxidants and pigments (of which carbon black is by far the most effective).

Polypropylene has increased sensitivity to oxidation due to the presence of substituted carbon atoms in the main chain. However, the higher crystallinity of polypropylene reduces access of oxygen to the vulnerable sites. Thus, antioxidants and ultraviolet absorbers which concentrate in the amorphous regions are effective in reducing photooxidation of polypropylene. However, the outdoor life expectancy cannot compare to the carbon black-filled polyethylenes. (15)

The addition of 2 to 3 percent carbon black and certain other pigments such as iron oxide, cadmium yellow, oranges, mercadmium reds in .5 - 2 percent concentrations are effective in improving ultraviolet stability. On the other hand, titanium dioxide appears to accelerate degradation.

For optimum results, it is essential that the stabilizers and pigments be small in particle size and finely dispersed in the resin system. The most effective ultraviolet absorbers are normally the substituted benzophenones or a derivative of salicylic acid of 0.25 - 1 percent concentrations. If color changes can be tolerated, a thermal antioxidant should be added to obtain a synergistic benefit with the ultraviolet absorber.

Best weathering results are obtained with a high density, high molecular weight, carbon black-filled polyolefin. In addition, certain polyethylene copolymers have superior ultraviolet stability over the homopolymers.

SECTION II. WEATHERING COMPONENTS VS POLYOLEFIN STRUCTURE

The term "weathering" is an all embracing term that includes the components of outdoor environment such as: solar radiation, temperature, oxygen, ozone, humidity, precipitation, wind, biological agents, dust and atmospheric chemical impurities. Any one or all of these components will vary with the geographical location and time and thus complicate the weathering effects further.

The effect of geographical location and season on the weathering of identical polyethylenes is well demonstrated in Figures 1, 2, and 3.

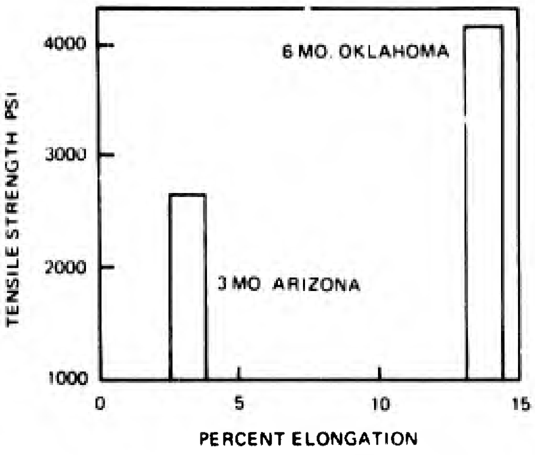

Figure 1. Effect of geographic location on unstabilized .960 density Marlex polyethylene resin (1)

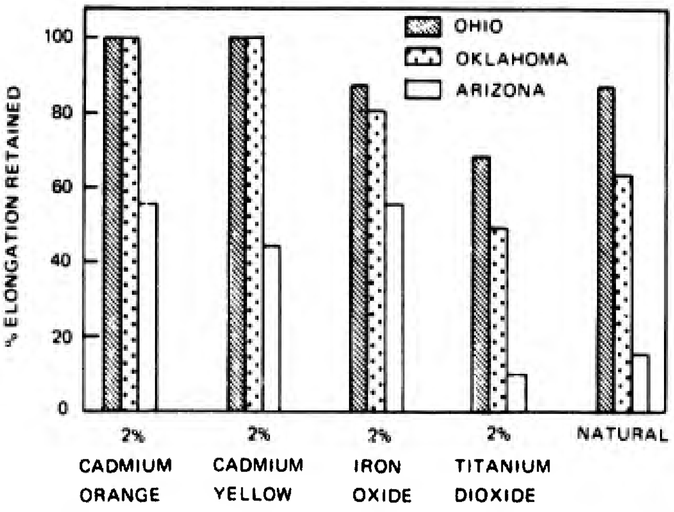

Figure 2. Comparative outdoor weathering data on Marlex polyethylene after one year of exposure (1)

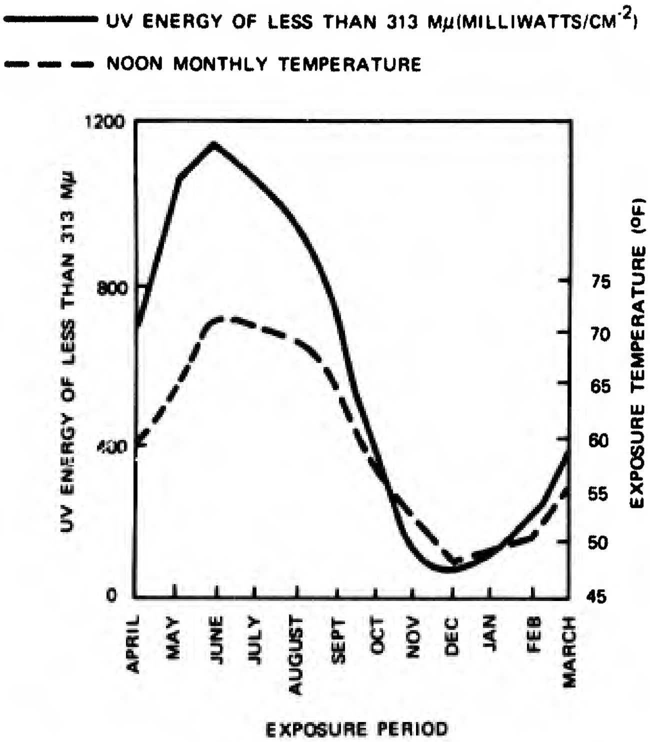

Figure 3. Seasonal effect upon UV energy and temperature in Arizona (2)

The degradation of polyolefins to outdoor exposure is not an additive effect of the above components but a complex interaction. The following briefly summarizes the effects of the major components on the polyolefin family.

- Moisture

As a general rule, stabilized polyolefins are not adversely affected by moisture. However, condensation below freezing can result in physical damage to the plastic surface. Also, condensation in jungle environments may promote the growth of fungi.

Moisture may affect unstabilized polyolefins undergoing degradation due to the presence of polar or functional groups. These groups, such as hydroxyl (OH) or carboxyl (COOH) are hydrophilic and may promote swelling.

Under some conditions rain may accelerate the surface erosion of protective coatings.

- Atmospheric Agents

Of all the atmospheric effects, oxygen is clearly the most damaging chemical agent. Unstabilized polyolefins are readily affected by both photo and thermal oxidation resulting in embrittlement, darkening and decrease in molecular weight. Although there are distinct differences in photo and thermal oxidation mechanisms (see Figure 4), the degradation is attributed to the breakdown of the carbon-hydrogen chain and depends on the morphology of the polymer.

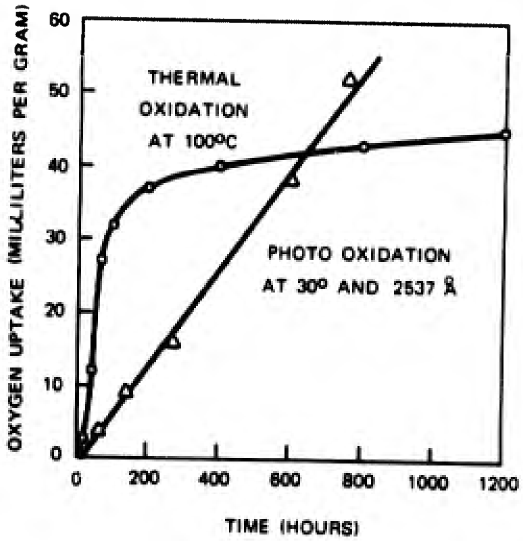

Figure 4. Oxygen absorption by linear polyethylene at 100°C in the dark and on exposure to radiation of 2537Å wavelength at 30°C(4)

The oxidation process can be divided into several steps; namely, induction (or initiation), propagation and termination. Immediately after contact with oxygen the induction period begins. There is a slow rate of oxygen uptake. This is followed by a slight rise in temperature and carbonyl and hydroperoxide compounds are formed.

In propagation, the next step, the oxygen absorption increases at an accelerated rate, the temperature rises explosively and there is a rapid formation of oxygen-containing groups initiated by energy sources (such as heat, radiation and light) or sensitizing impurities within the polymer.

The carbonyl and hydroxyl compounds formed during oxidation produce a high concentration of peroxides which decompose by free radicals and cause rapid oxidation. Depending on the differences in chemical structure, cross-linking or chain scission may occur. The frequent or regular occurrence of branching along a polymer chain increases the susceptibility of the polymer to oxidation. Therefore, polypropylene, which contains hydrogen atoms attached to tertiary carbon atoms, is more prone to oxidation than branched polyethylene which, in turn, is more readily oxidized than linear polyethylene. (See Figure 5.) The oxidation of polyethylene usually leads to crosslinking, whereas in polypropylene it results in depolymerization to low molecular weight products.

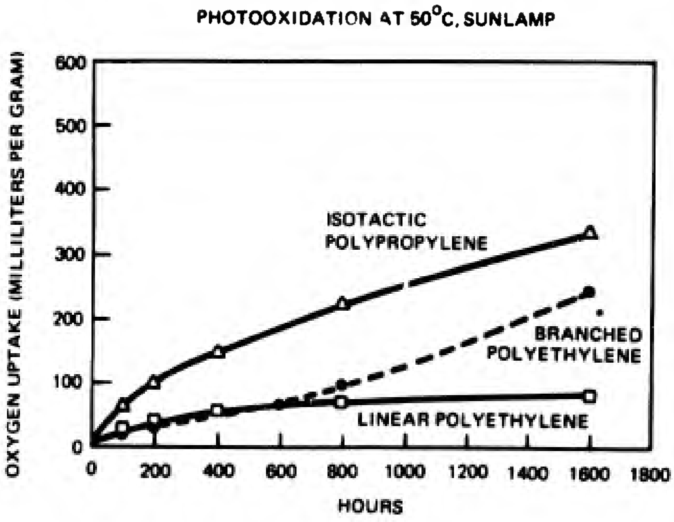

Figure 5. Exhaustive oxidation of polypropylene and branched and linear polyethylene under exposure to radiation of greater than 2800Å wavelength at 50°C. (4)

Note: Branched PE - Melt Index 0.3, Union Carbide DYNK
Linear PE - Melt Index > 0.001, Allied Chem Corp. AC-X
or
Linear PE - Melt Index 0.5, Phillip Petrol. Co. Marlex 600, type 5
Polypropylene - med. mole. wt experimental samples

The physical structure of the polymer also influences the amount of oxygen which reacts. The oxidation rates of two different polyethylenes, linear and branched, at the same temperature is demonstrated in Figure 6. Oxidation is

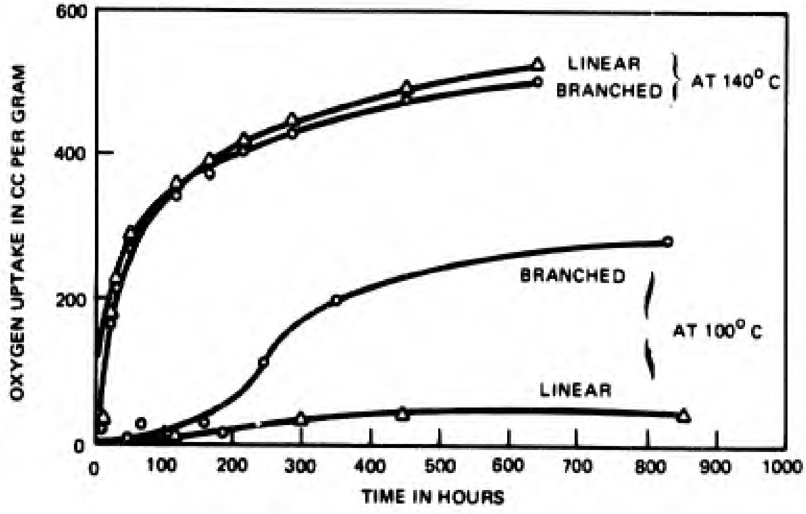

Figure 6. Oxidation of polyethylene above and below the melting point. (5)

more impervious to the crystalline or ordered regions than the disordered or amorphous regions. Since linear polyethylene is about 90 percent and branched a-about 60 percent crystalline, the oxygen uptake is about four times greater for the branched polyethylene. This effect is shown in the same Figure where at 140° both polyethylenes are amorphous. The oxygen uptake has increased about twice for the branched polyethylene and about 10 times for the linear polyethylene. (5)

Limited oxidation may improve the physical structure of some polymers. Figure 7 shows the rapid change in the density of polyethylene and polypropylene during reaction with 20 and 40 cc, respectively, of oxygen. This is attributed to a secondary crystallation process which occurs when a few polymer chains undergo oxidative cleavage and permits an additional degree of crystallation. (5) The second stage of increasing density shown in Figure 7 is attributed to the accumulation of oxygenated reaction products.

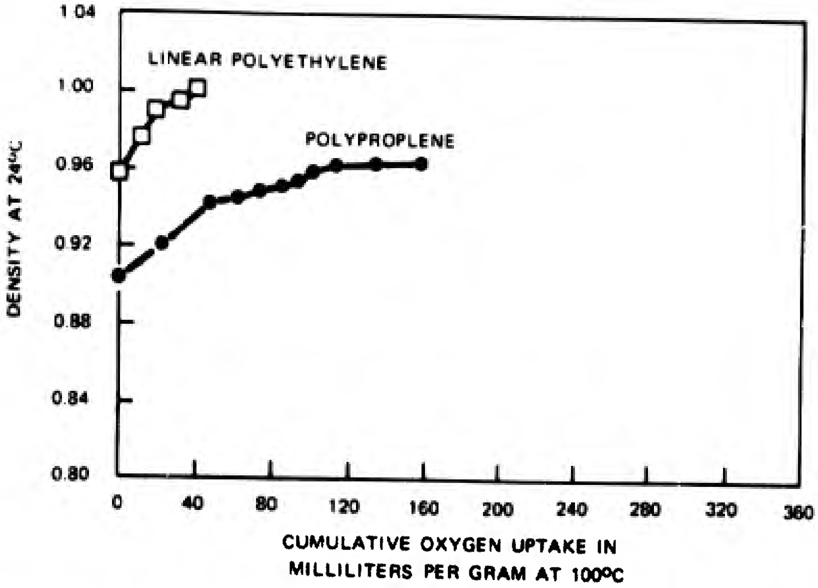

Figure 7. The relationship between density and cumulative oxygen uptake in various polyolefins. (5)

The degree of oxidation is dependent on the specimen thickness; the thinner the specimen the greater the oxidation degradation.

Metallic contaminants accelerate the thermal oxidation of low molecular weight polyolefins by catalyzing the breakdown of peroxides. This produces a higher concentration of radicals than the thermal decomposition process. Copper causes a rapid acceleration of oxidation in polypropylene. Copper, chromium, manganese and lead compounds produce a similar reaction in low density polyethylene.

The oxidative degradation of polyolefins can be inhibited by the addition of a variety of antioxidants, ultraviolet stabilizers and pigments. The reader is referred to Section IV, "Means of Stabilization", for further information.

Ozone (O_3) - Although ozone which is present in atmospheric concentrations from zero to a few parts in 10^7 readily attacks rubbers, it seldom damages polyolefins. This is due to their saturated main chains.

Dust, chemical impurities and other air-borne abrasives - These may have an effect on plastics. The effect of abrasiveness on the surface of the plastic depends on the hardness and resiliency of the plastic. Normally, polyolefins are only slightly damaged. Dust and noncorrosive particles can also act as a radiation screen. Contaminants such as sulfur dioxide, sulfur trioxide and nitrogen dioxide found in air pollution are usually not damaging to polyolefins.

Salt spray tests indicate that salt has little effect on polyolefins. However, salts may crystallize within the composition due to changes in temperature and humidity and cause crazing or cracking.

- Radiation Effects

Plastics are affected by the radiations from the electromagnetic spectrum. The energy of these radiations is determined by their frequency, which is inversely proportional to their wave length. As can be seen from the electromagnetic spectrum in Table 1, the long waves (such as radio) produce less energy than the shorter waves (x-ray).

TABLE 1. LIGHT ENERGY ACCORDING TO WAVELENGTH

Wavelength (mμ)	Type of Radiation	Energy of 1 Einstein (K cal.)
10,000+	Infra-red	2.86
700	Visible red light	40.9
500	Visible blue light	56.9
400-300	Ultraviolet	71.0-95.3
300-100	Ultraviolet	143.00-286.00
1-0.1	X-rays	2.86×10^4 - 2.86×10^5
0.01-0.001	Gamma rays	2.86×10^6 - 2.86×10^7

Energy from the long waves merely causes the polymer molecules to rotate and has little effect on the plastics. Radiation from the shorter waves (infrared) causes the molecules to vibrate and therefore produces heat. Polyolefins absorb electromagnetic radiation in the ultraviolet or 300 - 370 mμ wavelength and this energy results in the most damaging breakdown of the polymers causing discoloration, embrittlement, etc. Most of the energy of the very short (x-ray less than 300 mμ) range is absorbed in the atmosphere and has little influence on the polymer structure.

The bonds between carbon and hydrogen are strong but can be dissipated by the energy in ultraviolet radiation. The time for this deterioration appears to be proportional to the length of the polymer chain. (3)

When enough energy is absorbed in the form of photons carbonyl groups occur. This photo degradation process is attributed to free radicals produced either by photo decomposition of ketonic compounds or by activation of the hydrocarbon chain adjacent to the carbonyl group. The free radicals thus formed continue to react with oxygen to give peroxy radicals which propagate the degradation by the autoxidation mechanism.

Materials and mechanics for ultraviolet stabilization are discussed further in **Section IV**.

Photodegradation results in a reduction of molecular weight and consequently increases brittleness. Also, in high density polyethylene both crosslinking and scission occur simultaneously. Therefore, it will require a longer time for a high molecular weight resin to embrittle in the presence of ultraviolet radiation than a lower molecular weight material. This effect is illustrated in Figures 8 and 9 on compression molded tensile specimens which were exposed for one year in Arizona.

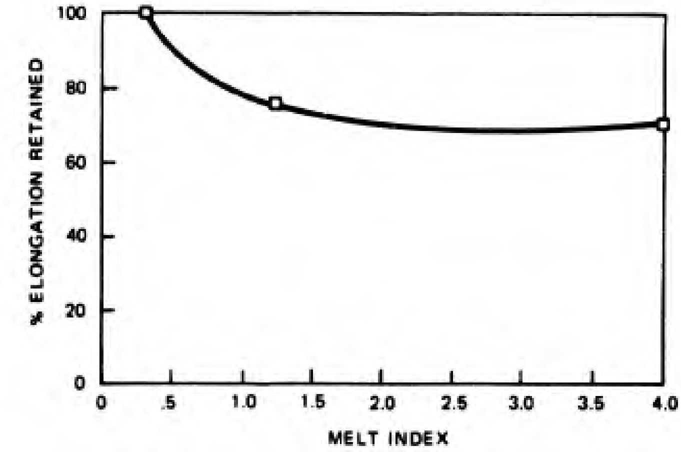

Figure 8. Effect of resin melt index on weathering performance of .95 density stabilized Marlex ethylene-butene copolymer after one year's exposure in Arizona (1)

Note: Molecular weight is inversely related to melt index.

The .3 melt index (or highest molecular weight) material did not lose any elongation in one year's exposure; however the 1.2 and 4.0 materials lost approximately 30 percent. (1)

It was pointed out previously that branched polyolefins will undergo thermal oxidation more readily than the more linear polyolefins. Figure 9 shows the results of artifical weathering on two different density materials - a 0.95 density ethylene-butene copolymer and a 0.960 polyethylene homopolymer - of similar melt indexes.

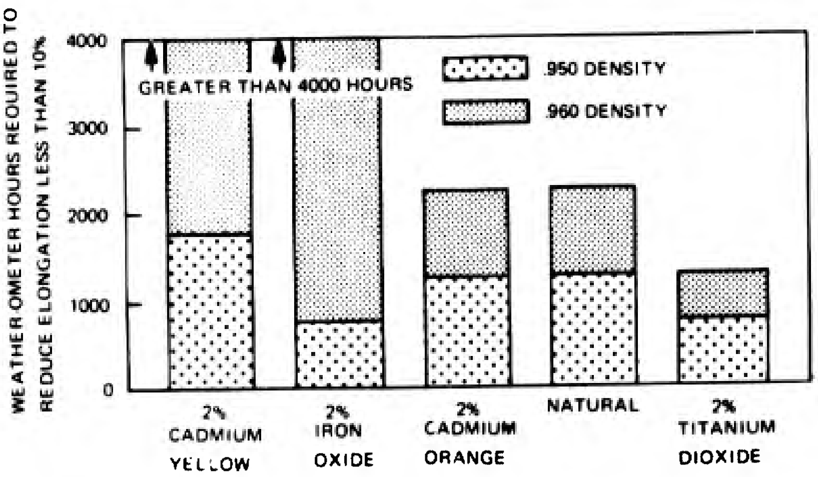

Figure 9. Effect of resin density on weathering performance of nominal 0.3 melt index compression molded Marlex samples after 4000 hours' exposure in Weatherometer (1)

As can be seen, the 0.950 density (or more branched) copolymer weathered significantly better than the 0.960 density homopolymer as evidenced by the reduced elongation. (1), (6)

Maximum absorption of radiant energy occurs on the surface of the polyolefins which contain a uniform distribution of absorbing groups. Therefore, thin films are more vulnerable to photo oxidation.

- Biological and Fungi Attack

Although biological and fungi attack are affected by weather and soil conditions, much of the information is categorized under the general subject of microbiological deterioration and not weathering. Therefore, this material will not be covered in this report. However, for the curious, Reference 46 reports on the exposure of 12, 12" x 1" polyethylene specimens at Port Harcourt (Jungle) and Kano, Nigeria (Desert) in termite-infested ground which was previously baited. After 11 months, the specimens were withdrawn. Pronounced nibbling occurred on many specimens and all seven cable covering materials tested had been nibbled to a slight degree.

Biological growth, principally algal growth, was heavy at the Jungle site and was heavier on the light colored sheets than those with carbon black.

- **Temperature**

Temperature has a profound effect on polyolefins. Because they are thermoplastic, they will soften with very warm temperatures and embrittle at low temperatures. Increasing temperatures also influence chemical reactions and therefore will accelerate thermal oxidation and ultraviolet degradation.

Figure 10 demonstrates how temperature changes during ultraviolet exposure affect polymer degradation. A 10°C temperature increase almost doubled the rate of degradation. (2) Therefore, exposure conditions involving different temperatures will result in poorly correlated data.

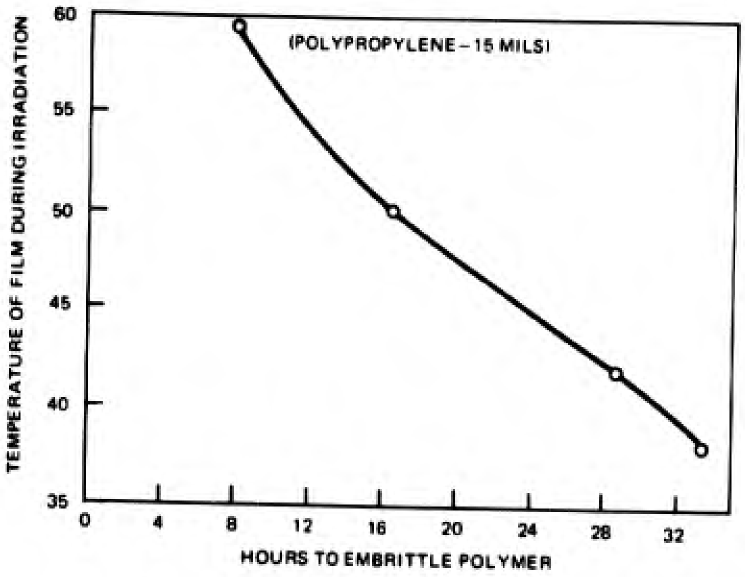

Figure 10. Temperature of film during irradiation vs. degradation time (Hanovia Hg. lamp with Corex D filter) (2)

SECTION III. EXPOSURE AND TESTING METHODS

As stated in the Introduction, the author does not wish to enter into the controversy concerning the merits of the various weathering testing methods. However, all weathering data are based on one or more of these methods and the reader should be familiar with the established method to properly evaluate the results. A brief listing of the more popular methods is given below:

Outdoor Exposure

- Mounted vertical, facing south
- Mounted five degrees from horizontal, facing south
- Mounted at same degree as latitude, facing south
- Mounted 45° from horizontal, facing south
- Mounted in stressed condition 45° from horizontal, facing south
- EEK - Follow-the-sun where angle changes with season and hour.
- EMMA - Follow-the-sun equatorial mount carrying 10 mirrors. Each mirror is 6" x 6' and reflects the sunshine onto the samples. The mirrors are about 80 percent reflective and therefore increase the solar energy about eight times.
- EMMAQUA - Same as EMMA but with an intermittent water spray to simulate rain.

Artificial Exposure Sources

- Sunshine carbon arc - The short wavelength radiation is modified by a Corex "D" glass filter.
- Enclosed carbon arc - The same as above but enclosed in a Pyrex glass globe.
- Fluorescent sunlamp
- Fluorescent blacklamp
- Xenon Arcs
- Hoffman Lamp - Composed of tungsten filament together with mercury vapor lamp
- Mercury Vapor Arcs

Artificial Weathering Instruments

- Xenotest - This is a 1,500 watt high-pressure xenon arc lamp with a water filter which removes a proportion of the infra-red radiation. A high speed fan cools the test samples to 30° - 35°C. Samples 3.93" x 1.77" (10 cm x 4.5 cm) are held in frames which rotate around the arc at a distance of 3" from the center and at 5 rpm. Sample frames rotate 180° so that both sides of holder can be used to hold samples and to simulate light and shade. Humidity by means of water sprays can be controlled up to 90 - 95 percent RH. (8)

- Fugitometer - This employs a carbon arc enclosed in a glass globe. No water filter is used and there is no humidity control. The samples held in frames which rotate around and are continuously exposed to the arc at a distance of 9".

- Fade-Ometer - A carbon arc with controlled temperature and humidity.

- Weather-Ometer - An enclosed carbon arc employing water sprays to completely wet samples in the presence or absence of radiation. Humidity can be controlled between 20-60 percent RH and the black panel temperature between 60° and 90°C. A xenon lamp can be used instead of a carbon arc.

Standard Exposure Test Methods

- Outdoor Weathering of Plastics - ASTM 1435; USSR Std No. 10226-62
- Resistance of Plastics to Artificial Weathering Using Fluorescent Sunlamp and Fog Chamber - ASTM 1501; Fed. Std. 406, Method 6024

- Operating Light and Water-Exposure Apparatus (Carbon-Arc Type) for Artificial Weathering Test - ASTM D 1499; E 42-64

- Accelerated Weathering of Plastics Using S-1 Bulb and Fog Chamber - ASTM 795

- Resistance of Plastics to Sulfide Staining - ASTM D1712 - 60 T

- Accelerated Weathering, Carbon Arc Without Filters; Alternate Navy Test - Fed. Std. 406, Method 6022

- Accelerated Weathering; soaking, freezing, drying, Ultraviolet Cycle, Alternate Navy Test - Fed. Std. 406, Method 6023

- Colorfastness to Light - Fed. Std. 406, Method 6031

- Accelerated Yellowness - Fed. Std. 141, Method 6132

- Salt-Spray Test - Fed. Std. 406, Method 6071

- Recommended Practice for Operating Xenon Arc-Type Water-Cooled Light and Water Exposure Apparatus for Exposure of Plastics ASTM D 2565-66T

Figure 11 compares various artificial light sources with global radiation. Global radiation is defined as the radiation between 315 and 800 μ falling on a horizontal plane from sun and sky on flat country on a cloudless day. (8)

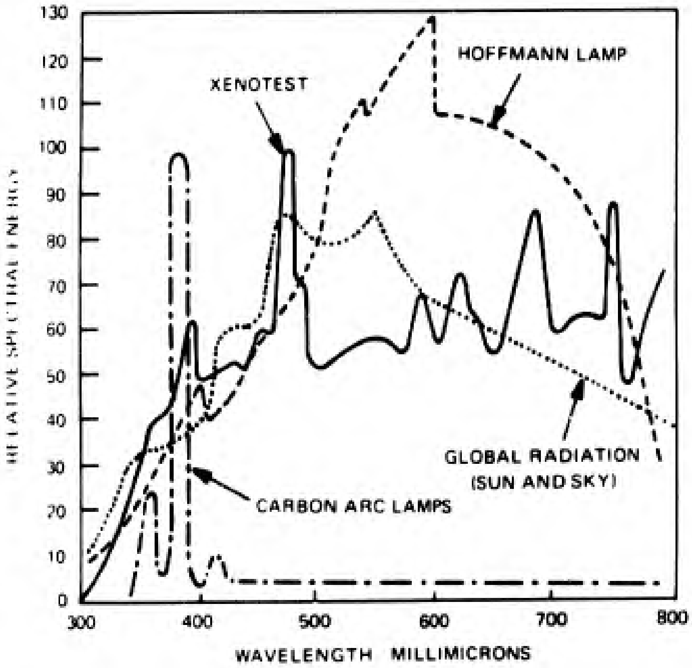

Figure 11. Spectral energy distribution in various types of illumination (8)

A comparison of the natural solar radiation received, in Langley's,* with the exposed sample angle is illustrated in Figures 12 and 13.

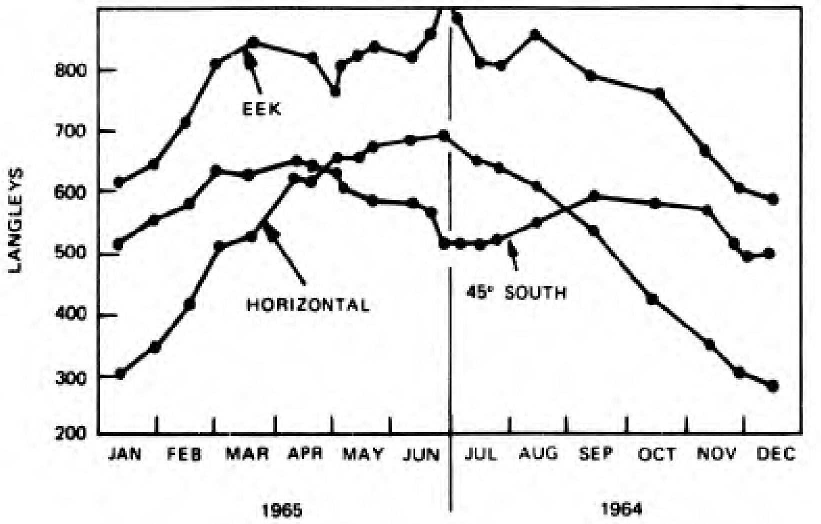

Figure 12. Comparison of radiation at various angles in Phoenix, Arizona (9)

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* Langley=total solar radiation as measured in gram-calories/cm^2.

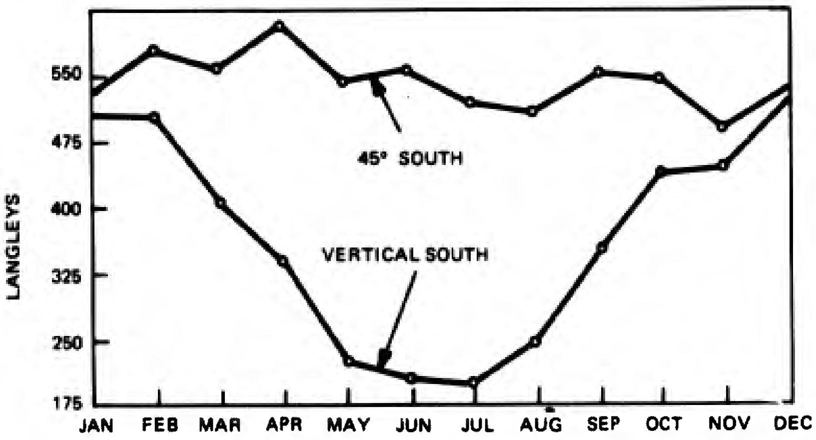


Figure 13. Monthly variations in solar radiation at Phoenix, Arizona (9)

There is a greater amount of sunlight radiation incident on a 45° south rack than on a vertical rack facing south (except in the Arctic). Also, the farther south the location, the greater the increase in sunlight. For example in Seattle (48° north latitude) the ratio of intensity between vertical and 45° south is 0.74 whereas in Key West (24° north latitude) the ratio is 0.41. (9)

Figures 14 through 18 compare the ultraviolet spectral distributions of the artificial exposure sources with those of natural sunlight below 4000Å.

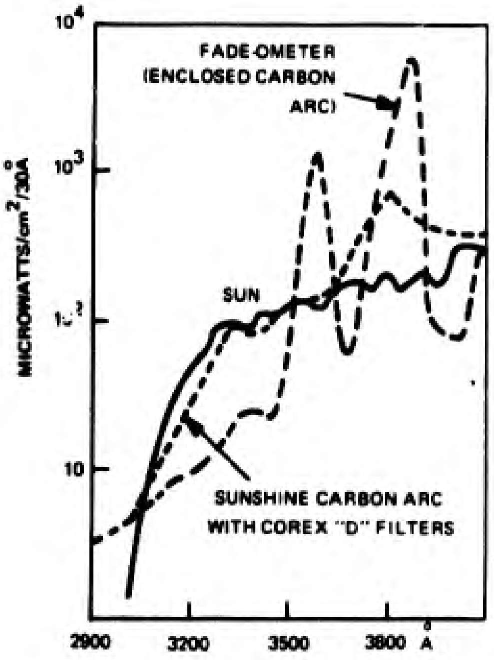


Figure 14. Ultraviolet spectral distributions of the enclosed carbon arc Fade-Ometer, and sunshine carbon arc compared with sunlight (10)

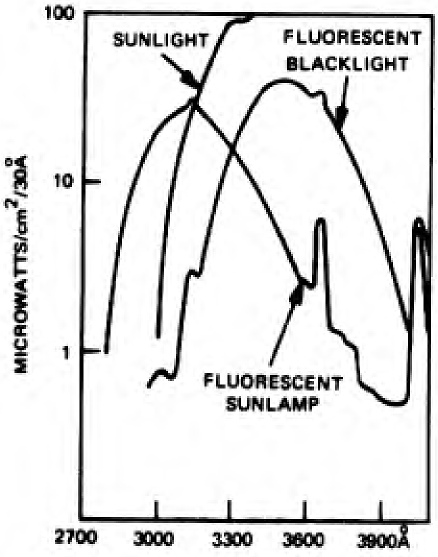


Figure 15. Ultraviolet spectral distributions of the fluorescent sunlamp and fluorescent blacklight (10)

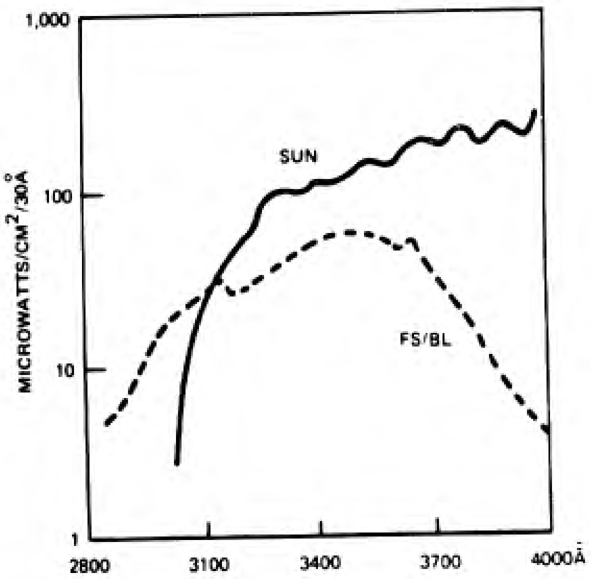


Figure 16. Combined spectral energy distribution of FS-type sunlamp and BL-type black light (11)

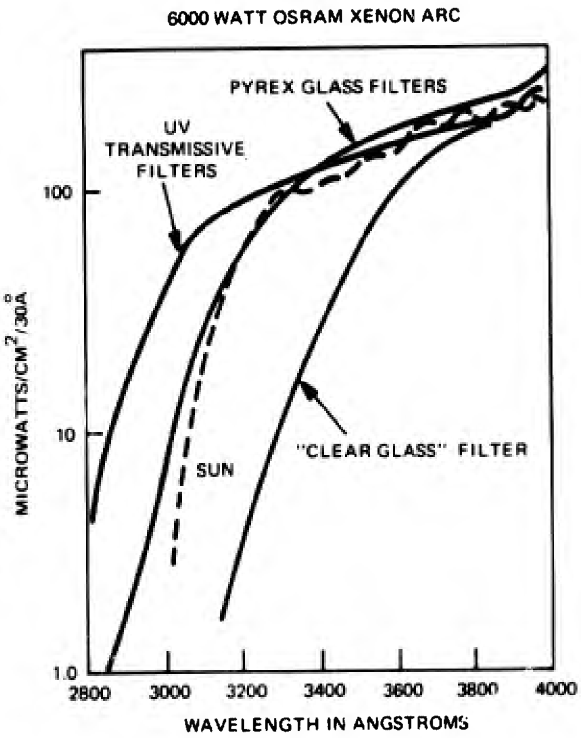


Figure 17. Spectral energy distribution of 6000 watt Xenon Arc (11)

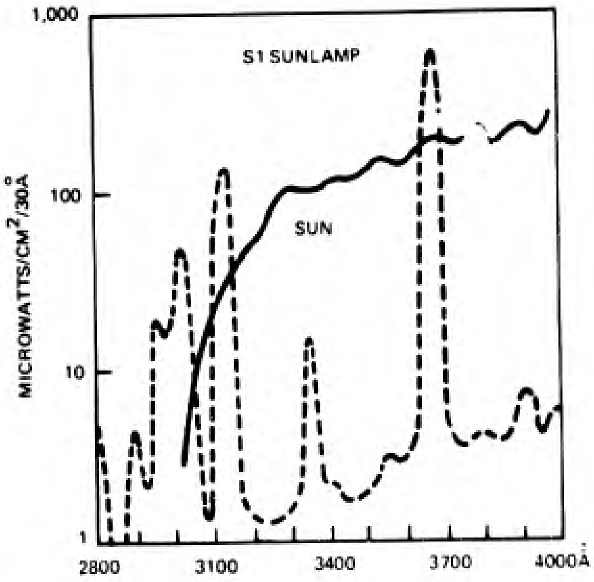


Figure 18. Spectral energy distribution of S-1 (Mercury) sunlamp and natural sunlight below 4000Å (11)

From these figures the following can be concluded:

- The enclosed carbon arc imparts intensity far in excess of that of sunlight above 3500Å and considerably less than sunlight at the shorter wavelengths (under 3500Å).

- The sunshine carbon arc imparts close approximation to natural sunlight to about 3600Å but also imparts greater intensity than sunlight above 3600Å.

- The fluorescent sunlamp has considerably less intensity than sunlight in the longer wavelengths (above 3130Å) and more intensity in the shorter wavelengths (under 3130Å).

- The fluorescent blacklamp's emission peaks at about 3520Å and its intensity is considerably less than natural sunlight above 3050Å.

- Combining the two fluorescent lamps shifts the emission peak to 3650Å and gives a closer approximation to the natural sunlight than either lamp alone.

- The 6000 watt xenon arc with the Pyrex glass filter gives the closest approximation to the natural sunlight.

- The S-1 mercury arc sunlamp has greater emission than sunlight in the short wavelength (below 3200Å). The overall correlation between sunlight and S-1 emission is poor.

Due to the variations in the ultraviolet radiation emitted by the different weathering methods, a wide dispersion in data can be obtained.

An example of the effect that different exposure methods can have on weathering data is illustrated in Figure 19. Two polypropylene monofilaments, one

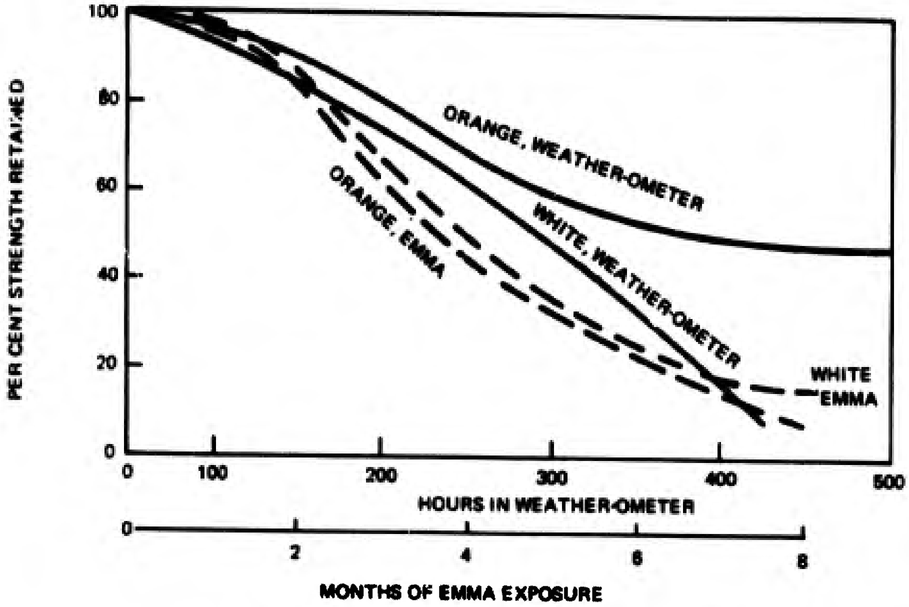


Figure 19. Results of EMMA and weather-ometer exposure on white and orange polypropylene monofilament (12)

white and the other orange, were exposed in EMMA and 500 hours in a Weather-Ometer. No correlation of the data can be made between the two exposures since the white formulation was superior to the orange in EMMA but inferior in the Weather-Ometer. Similar conflicting data have been reported on polyethylene tensile specimens. (12)

Table 2 lists some of the advantages of Outdoor and Accelerated Tests.

Some of the popular parameters for determining the degree of weather degradation are:

Melt index
Carboxyl content and/or absorption
Intrinsic viscosity
Ultraviolet absorber concentration

Change in color
Surface crazing or cracking

Tensile strength
Elongation
Flexural strength
Brittleness temperature

Manual bend
Impact strength

Power factor
Dielectric constant
Dielectric strength

The first group aid in identifying changes in chemical structure such as crosslinking, oxidation and chain-scission. Changes in appearance are often used to indicate a decline in mechanical properties.

The mechanical properties usually determine the life of a part. Elongation is a sensitive criterion for weather deterioration in that it declines much faster than strength. For instance, the tensile strength can be quite high when elongation has almost disappeared and the material has become brittle.

Special properties such as for electrical applications are determined by dielectric strength, constant and power factor.

The degree of weathering which can be tolerated depends on the property involved. Table 3 compares the hours required for failure by various test methods for a stabilized and unstabilized ethylene-butene 1-copolymer.

In summary, the polymer structure, the properties of interest, the selected test methods and the type of exposure all influence the weathering data obtained.

TABLE 2. ADVANTAGES OF OUTDOOR EXPOSURE AND ACCELERATED TESTS (13)

Outdoor Exposure	Accelerated Tests
The spectral distribution of the normal sunlight is not reproduced in the artificial equipment. While the claim is made that noon June sunlight is approximated, a material outdoors sees June noon sunlight only a small fraction of each year. Factors other than moisture, temperature, and sunlight have a bearing on how well a material endures. Passing through critical temperature ranges, e.g., the freezing point of water, the accumulation of atmospheric impurities such as dust and industrial fumes, the damage resulting from hail, and many other factors are eliminated in the laboratory. Materials will vary according to their spectral distribution absorption characteristics and their sensitivity to various wavelengths. Thus two materials exposed at the same time in the same machine may be ranked incorrectly. While a correlation between artificial and outdoor weathering for compounds varying only slightly can be established, in order to do so the outdoor exposure must be conducted. Thus, the elapsed period has not really been shortened. For many locations, the yearly average rainfall, solar radiation, dust fall, etc., are quite consistent even though significant fluctuations occur over shorter periods of time. The general state of the art is indicated by numerous attempts to modify and improve commercial equipment. Since sunlight is not continuous, there is an opportunity for free radicals to decay and volatile decomposition products to vanish. The retention or loss of degradation products on the surface of the sample is not duplicated in the laboratory. Outdoor conditions may not provide the minimum required energy to initiate some reactions. Laboratory lamps are of high intensity and mounted close to the sample. Therefore samples are subjected to considerable heat. Even with cooling fans the actual temperatures of the samples may be much higher than many outdoor exposures.	Information can be gathered much faster. Control of exposure conditions is more precise and reproducible. For systems with minor variations (such as changing only the stabilizers in a system) relative rankings can be assigned with a good expectation that the rankings would be maintained outdoors. If a system deteriorates quickly under artificial conditions, the potential for outdoor use is very slight and no more time need be wasted. Equipment of this type is quite useful for showing that the manufacturing process is or is not under control, i.e., the product is uniform from time period to time period. It also serves the same purpose when inserted in a purchase document or specifications. Since the testing time is shortened, the exposure period can continue to the point where the judgment needed by the operator is minimized. This allows use of less highly trained personnel. Within limits, the special distribution, the temperature and the moisture can be adjusted to represent a wide range of climates with none of the expense and time involved in exposing specimens in the varying climates outdoors. The procurement and maintenance of measuring devices and recorders required to establish the exposure environment at the outdoor site is eliminated.

TABLE 3. A COMPARISON OF HOURS TO FAILURE FOR VARIOUS TEST METHODS IN AN ATLAS XW WEATHER-OMETER (12)

Test Procedure	Hours to Failure	
	With UV Absorber*	Without UV Absorber
Tensile Strength to 2/3 Original Value	1,050 Hrs.	250 Hrs.
Elongation to Absolute Value of 10%	800 Hrs.	225 Hrs.
Brittleness Temperature, -50°F	400 Hrs.	125 Hrs.
Bent Strip, F_{50}	1,000 Hrs.	260 Hrs.

*U. V. Stabilizer 0.1 UV-531, a substituted benzophenone

SECTION IV. MEANS OF STABILIZATION

Antioxidants

Polyolefins are saturated hydrocarbon polymers and are therefore more resistant than unsaturated polymers to oxidation. But they do oxidize rapidly at elevated temperatures and in thin films during processing and weathering. Polypropylenes, as previously stated, because of their structure are extremely susceptible to oxidation during processing and more susceptible than polyethylene in normal use.

Antioxidants for the inhibition of thermal oxidation are classified as follows:

- Propagation suppressors and inhibitors:

Hindered phenols and secondary aromatic amines function as effective antioxidants by reacting with the propagating radicals described in Section I to interrupt the oxidative chain. However, the latter are not generally used because they impart color to the polymer after short exposure to oxygen.

These chain terminating labile hydrogen antioxidants function by a sacrificial role. When they are exhausted oxidation becomes autocatalytic and eventually reaches a rate similar to the uninhibited polymers. (5)

- Peroxide deactivators

Stabilization systems based on antioxidants possessing no labile hydrogen include thiodipropionate esters, organic sulfides, disulfides and esters of phosphorous and boric acid. These function by their ability to deactivate peroxides and prevent their decomposition into radical products.

Synergism

The phenomenon known as synergism is prominent in stabilizing polyolefins. This phenomenon occurs when certain stabilizers are combined to provide greater life expectancy than would be obtained from the sum of each stabilizer. (See Figure 20.) For example, combining a hindered phenol and sulfide will produce chain termination through the labile hydrogen of the phenolic group as well as peroxide deactivation by the sulfide. Thus, oxidation is inhibited in two stages. The chain terminator reduces the length of the oxidative chain by terminating the propagating radicals. This reduces the amount of peroxide formed which must be deactivated. In turn, the peroxide deactivator controls the accumulation of radicals which would eventually consume the chain terminator.

Organo-sulfur compounds exhibit synergistic behavior with the hindered phenols since they decrease the number of radicals with which the phenol must contend. (16)

This synergistic oxidative behavior has also been evidenced by the addition of dilauryl thiodipropionate (DLTDP) to polyolefins containing a hindered phenolic antioxidant. Several-fold increases in resistance to thermal oxidation have been studied in polypropylene over a wide range of temperature. (17) However, it suffers from susceptibility to extraction by water. (18)

Distearylthiodipropionate (DSTDP) is reported to show higher synergistic activity than DLTDP. Trilauryl trithiophosphite has been made available recently for improved color and purity. (18)

This synergistic effect also occurs when combining antioxidants with ultraviolet stabilizers (Figure 21) and pigments and will be discussed further under those subjects.

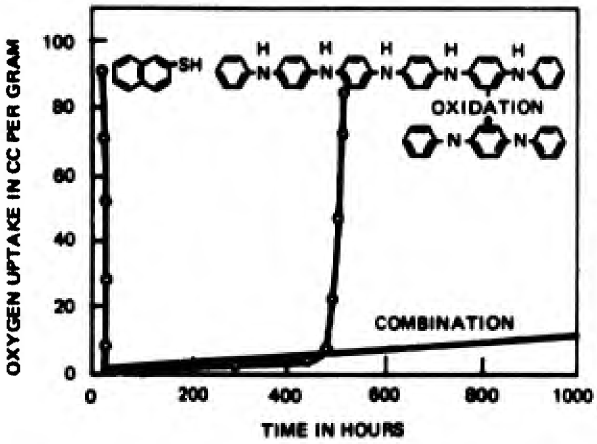


Figure 20. Synergism in polyethylene stabilization using 0.1% of 2-naphthalenethiol and 0.1% of N, N'-diphenyl-p-phenylenediamine at 140°C. (5)

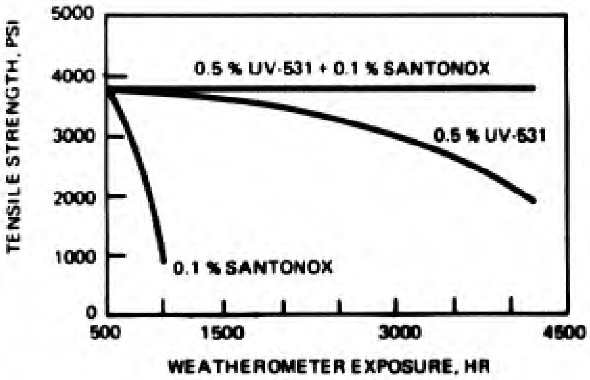


Figure 21. Synergistic effect of 0.5% UV 531 and 0.1% Santonox (19)

Table 4 presents a list of some common polyolefin antioxidants.

The effectiveness of various antioxidants in low-density polyethylene was compared at 110°C by measuring the induction period to produce an arbitrary change in the infra-red absorption due to carbonyl groups at 5.84μ. This work covered more than a hundred antioxidants and some of the results are summarized in Table 5. (15)

The choice of type and amount of antioxidant is determined to a large extent on the susceptibility of the polyolefin structure to oxidation. The stabilizer requirements normally increase in the series, high-density polyethylene, low-density polyethylene, ethylene-propylene copolymers and polypropylene.

Table 6 compares the increased stabilizer requirements of polypropylene with low-density polyethylene.

Compatibility and volatility of the various antioxidant systems are important. It has been found that the less polar polyethylene has lower tolerances for stabilizers than the more polar polypropylene.

TABLE 4. POLYOLEFIN ANTIOXIDANTS

Amines

Diphenylamine
Phenyl-α-naphthylamine (neozone A)
Phenyl-β-naphthylamine (neozone D)
Mixture of neozone A and diphenyl-p-phenylenediamine
Diphenyl-p-phenylenediamine
N, N'-phenylcyclohexyl-p-phenylenediamine
N, N'-di-β-naphthyl-p-phenylenediamine

Phenols

p-Hydroxyphenylcyclohexane
Di-p-hydroxyphenylcyclohexane
Dicresylolpropane
Mixtures of alkylated phenols
2,6-Di-tert-butyl-4-methylphenol
2,4,6-Tri-tert-butylphenol
Condensation products of dialkylphenols with formaldehyde
Reaction products of phenol with styrene
1,1'-Methylene-bis-(4-hydroxy-3,5-tert-butylphenol)
2,2'-Methylene-bis-(4-methyl-6-tert-butylphenol)
2,6-(2-Tert-butyl-4-methyl-6-methylphenol)-p-cresol
Phenylethylpyrocatechol and phenylisopropylpyrocatechol
2,2'-Thio-bis-(4-methyl-6-tert-butylphenol)
4,4'-Thio-bis-(3-methyl-6-tert-butylphenol)
1,1,3 tris (2'-methyl-5'-t-butyl-4-hydroxy-phenyl) butane
2,2-methylene bis [6-(α-methyl cyclohexyl)-4-methyl phenol]
1,3,5-trimethyl-2,4,6-tris (3',5'-di-t-butyl-4-hydroxybenzyl) benzene

Sulfur-Containing Compounds

4,4'-Thio-bis-(3-methyl-6-tertbutylphenol)
Thio-bis-(β-naphthol)
Thio-bis-(N-phenyl-β-naphthylamine)
Methylthio-2-naphthalene

diphenylsulfide
Diphenyl disulfide
3-Tolyl disulfide
1-Dodecyl disulfide
Polymeric 1,10-decanedithiol

2-Toluenethiol
2-Naphthylthiol
Mercaptobenzothiazole
1-Dodecyl mercaptan

Phenylbenzyl sulfide
2,2'-tert-Butyl-4-methylphenol sulfide
Tetramethylthiurammonium sulfide
Tetramethylthiuram disulfide
2,2'-Diphenyldiamine disulfide
4,4'-Diphenyldiamine disulfide
Mercaptobenzimidazole
α-Naphthol
di-β-naphthyl sulfide
methyl-β-naphthyl sulfide
2,2'-thio-bis-(4-methyl-6-tert-butyl phenol)

Others

2,6-di-tert-butyl-4-methylphenyl
ester of pyrocatecholophosphorous acid
phosphite of α-naphthol and pyrocatechol
Carbon blacks

TABLE 5. EFFECTIVENESS OF ANTIOXIDANTS IN LOW-DENSITY POLYETHYLENE (15)

Antioxidant	Induction period 110°C. (days)
4-tert-butyl phenol	0·5-1
2,6-di-tert-butyl-4-methyl phenol	0·5-1
Bis-(4-hydroxy phenyl) 2,2'-propane	1
Bis-(2-hydroxy-3-tert-butyl-5-methyl phenyl) methane ...	10
4,4'-thiobis (3-methyl-6-tert-butyl phenol)	12
p-phenylene diamine	1·5
N,N'-diphenyl p-phenylene diamine	14
Agerite Resin D	25

TABLE 6. COMPARISON OF STABILIZER REQUIREMENTS (15)

	Antioxidant concentration (%)	Induction period (hours)
l.d. polyethylene	0	4
l.d. polyethylene	0.1	1000
polypropylene	0	1-2
polypropylene	0.5	400

Note: A comparison of induction periods of low-density polyethylene and polypropylene at 140°C in oxygen at a pressure of one atmosphere, using 4-4'-thiobis (3-methyl-6-tert-butyl phenol) as the antioxidant.

Carbon Blacks

Carbon blacks, besides being a pigment, light screener, etc. can also function as a thermal antioxidant (alone or synergistically with other compounds). They are usually classified into the following groups:

- Channel blacks (gas)
- Furnace blacks (gas, gas and oil, and oil)
- Thermal blacks (gas)
- Regal blacks (class of oil furnace blacks)

The effectiveness of carbon blacks as stabilizers are influenced by the following factors:

- Structure of the carbon black -

The structure, i.e. the tendency of the individual primary particles of carbon black to be associated into a chain-like network, varies. Some carbons prefer to be by themselves, others group together like grapes and others appear to string out in chains. Those which form a grapelike type of agglomeration are more average and are classified as "normal structure blacks". Those which are by themselves are referred to as "subnormal structure" and those in chain-like formation are considered as "high structure".

The channel and gas furnace blacks have a normal structure. The oil furnace blacks have a higher degree of structure than the gas blacks. The Regals (a special oil furnace black) are classified as low structure blacks. Thermal blacks have a subnormal structure. Generally, low structure blacks reflect less light than higher structure furnace black of the same particle size.

- Particle size

Particle size effectiveness varies with the radiation wavelength, i.e., the size of the particle increases as the wavelength increases. Particle sizes of 10 - 20 *u* in diameter are reportedly the most effective for polyolefins. (See ultraviolet stabilizers.) Channel black particles have a relatively narrow and normal distribution whereas furnace blacks tend to have a broad distribution and are often skewed. (20) In the case of two types of carbon blacks with the same particle size and weight, the furnace black with a broader distribution would produce a larger number of coarser particles than the channel black.

- Percent of carbon black concentration

The effectiveness of carbon black as a thermal stabilizer continues to increase with concentration. This is in contrast to light screeners where optimum protection is reported at 2 - 3 percent concentration. (See Figure 22.) (21)

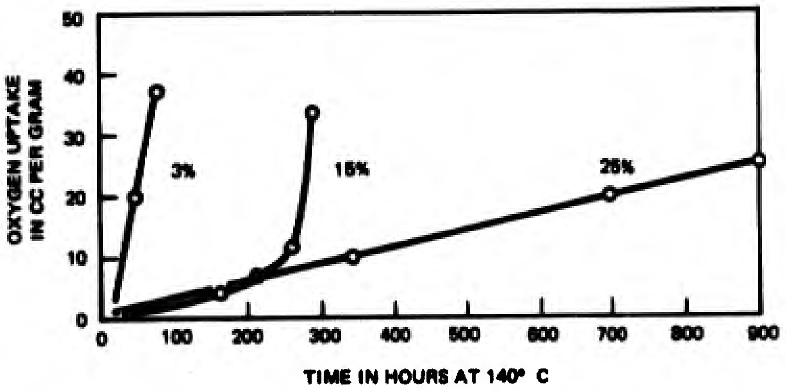


Figure 22. Effect of carbon black concentration on the oxidative stability of polythene (21)

- Size and arrangement of carbon black aggregates

Carbon blacks, dispersed in polyolefins, form agglomerates or kinetic units of larger dimensions than the dimensions of the primary particles. This is also influenced by the surface energy arising from the dimensions of the primary particles. Maximum effectiveness is obtained when these agglomerates are evenly dispersed throughout the polymer and are of optimum size.

- Surface chemistry

Carbon black particles vary in the population and nature of oxygenated structures combined with their surface. Some have little chemical activity but others act as weak or strong acids. All of the neutral surface structures are either quinones or acid derivatives (lactones, esters, etc.). Acid groups are attributed to carboxylic and hydroxylic acid structures. Channel blacks, because of their high concentration of polar groups, have more acidic surfaces than the furnace blacks. The acidic carbon blacks function as antioxidants by accepting polymer radicals, thus terminating chain reactions. (20)

- Dispersion

Since carbon blacks are insoluble in virtually all substances, the arrangement and distribution of the primary particles and aggregates is critical for good stabilization. Generally, due to the above factors, furnace blacks are inferior to channel blacks as antioxidant stabilizers.

Carbon blacks which have been activated by heating in an oxygen atmosphere to obtain a higher concentration of chemically combined oxygen on the carbon surface are considered to act as a giant phenol. However, the effectiveness between oxygen content and antioxidant effectiveness, although increased, is not a linear function as shown in Figure 23. (21)

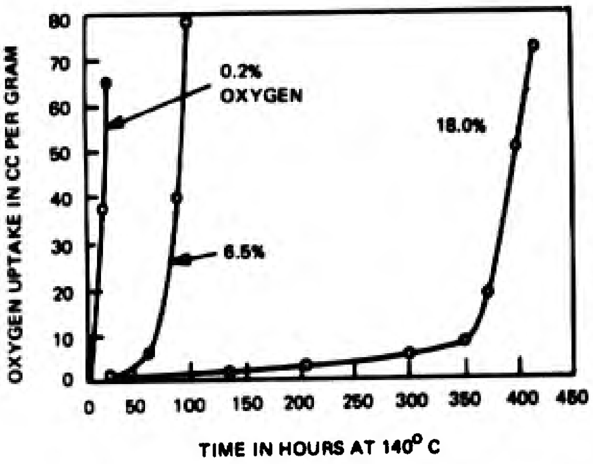


Figure 23. Effect of combined oxygen content on the ability of carbon blacks to inhibit thermal oxidization of polythene (21)

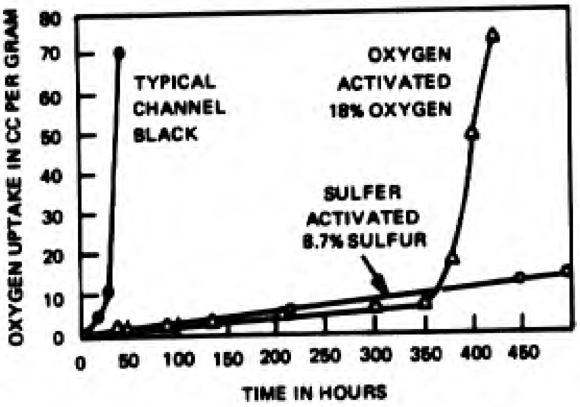


Figure 24. Activated carbon blacks as antioxidants for polyethylene at 140°C (5)

Also, when carbon blacks with polar surfaces are heated with elemental sulfur at high temperatures (550°C) chemical bonding results with about 6 to 8 percent sulfur. This activated carbon black functions as an effective peroxide decomposer, limiting polyethylene oxidation to a slow steady rate. Figure 24 shows no autocatalysis for over 500 hours. It has been reported that acidic carbon black also accepts polymer radicals and thus functions as a chain terminator as well as peroxide deactivator. (5)

Carbon black in combination with thiobis (2-naphthol) acts synergistically to minimize the tendency of polyethylene to undergo thermal degradation. Also, aliphatic thiols and disulfides which are not very effective antioxidants in clear polyethylene are reported good when combined with carbon black. (20) Some synergistic effects of carbon blacks with different antioxidants are given in Table 7.

TABLE 7. THERMAL STABILITY OF POLYTHENES CONTAINING CARBON BLACKS AND DIFFERENT ANTIOXIDANTS (23)

Type of black (C=channel, F=furnace)	Particle size (milli-microns)	pH	Oven ageing life* with 0.2 phr antioxidant		
			di-naphthyl-p-phenylene diamine (h)	4:4'-thiobis (3-methyl-6-tertbutyl phenol (h)	N-stearoyl-p-amino phenol (h)
Monarch 74 (C)	17	5·0	2250	3600	3400
Elf 8 (C)	29	4·5	1660	>3600	1380
Statex 160 (F)	17	8·0	1960	2800	2570
Vulcan 9 (F)	20	-	>3600	>3600	>3600
Vulcan 6 (F)	23	-	>3600	1610	1970
Vulcan 3 (F)	29	8·5	>3600	>3600	>3600
Sterling SO (F)	41	9·0	>3600	>3600	2500
No black	No anti-oxidant 800 h		>3380	2500	>3380

*Number of hours at 120°C required to reduce flex value by 50%.

In contrast it has been reported that amine antioxidants such as diphenyl-p-phenylenediamine are adversely affected by carbon blacks of small particle size with acidic surface, but are affected to a lesser extent by nonpolar furnace blacks. (22, 21)

A significant advantage in combining carbon blacks with conventional antioxidants is the ability of the carbon black to withstand evaporation or extraction. As demonstrated in Figure 25, little protection is lost by the evaporation of the antioxidant.

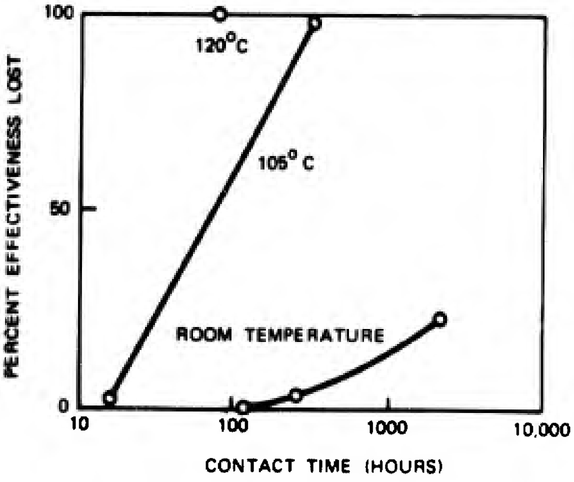


Figure 25. Loss of 4, 4'-thiobis-(3-methyl-6-tert-butyl phenol) from polythene during evaporation (subjected to a stream of nitrogen for 2 weeks at 105°C) (21)

Oxidative Catalysts

The presence of various metallic contaminants accelerates the thermal oxidation of low molecular weight polyolefins by catalyzing the breakdown of hydroperoxides resulting in a higher concentration of radicals. Copper or copper compounds cause rapid acceleration of the oxidation process in polypropylene. Copper, chromium, manganese and lead compounds result in a similar effect in low-density polyethylene. This effect even takes place when some antioxidants are present as illustrated in Table 8.

TABLE 8. EFFECT OF ANTIOXIDANT CONCENTRATION ON THE STABILITY OF POLYPROPYLENE (16)

Antioxidant* % by wt.	Induction Period at 140°C., in Hours	
	Copper Absent	1.5% by wt. Copper Dust
0	1.7	0.5
0.1	30	-
0.5	650	133
0.75	515	146
1.0	590	188
1.5	810	195

*The antioxidant is 6,6'-di-tert.butyl-4,4'-bis-o-cresol.

There are several types of complexing agents which can inhibit copper-catalyzed oxidation. The effectiveness of some copper inhibitors in polypropylene containing antioxidant systems is shown in Tables 9 and 10.

Again, it is pointed out that polypropylene requires a greater amount of antioxidant than polyethylene for equal stabilization. Thus, the loss of an appreciable portion of antioxidant results in greater oxidation. This loss of antioxidant can occur, for example, by extraction when polypropylene is placed in indiscriminate contact with other materials. Figure 26 illustrates the loss of stability of a commercially stabilized polypropylene after contact with a plasticized polyvinylchloride.

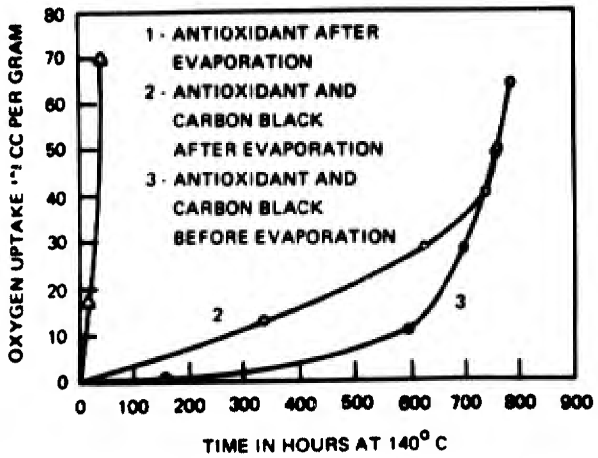


Figure 26. Loss of stability of polypropylene after contact with plasticized PVC. (16)

TABLE 9. COMPARISON OF COPPER INHIBITOR EFFECTIVENESS[1] (16)

Copper Inhibitor (0.5% by wt.)	Induction Period (Hours at 140°C)	Relative Volatility[2] Temp. (°C) for Wt. Loss of:		
		1%	5%	10%
None, no copper	1040	-	-	-
None	175	-	-	-
Oxamide	250	196	217	226
Oxanilide	436	215	234	243
Nylon 62	458		Decomposes above 300°C	
Malonanilide	290	240	250	254
Oxalyldihydrazide	630	209	221	227
Dicyclohexanone oxalyldihydrazone	515	202	218	229
Maleic acid hydrazide	463	217	241	253
Benzhydrazide	266	146	167	178
Salicylhydrazide	451	152	168	176
Isonicotinic acid hydrazide	407	173	189	196
p-Nitrobenzhydrazide	745	212	230	240
m-Nitrobenzhydrazide	927	199	217	230
Benzaldehyde semicarbazone	470	215	228	233
Benzotriazole	605	156	174	184
5-Chlorobenzotriazole	492	161	178	190
5-Methylbenzotriazole	715	164	183	193
5-Nitrobenzotriazole	>530	178	202	221
1,2-Naphthotriazole	>530	188*	208*	218*
5,6-Dimethyl-1H-benzotriazole	>530	171*	195*	205*
Benzazimide	531		Decomposes about 190°C	
1,2,4-Triazole	>530	113	132	141
3-Amino-1,2,4-triazole	927	165	191	203
3-(2-Pyridylmethylamino)-1,2,4-triazole	647	202	227	242
5-Amino-1,3,4-triazole	957	177	194	205
1,3-Diphenyltriazene	436	135	155	165
3-Hydroxy-1,3-diphenyltriazene	264		Decomposes about 120°C	
4-Hydroxybenzotriazene	448	177	194	201
4,4'-Biphenylenebis(3,3-dimethyl-1-triazene)	332	221	235	248
3-(p-Nitrophenyl)-1-(p-phenylazophenyl)triazene	352		Decomposes about 210°C	
3-Anilino-1,4-diphenyl-5-phenylimino-1,2,4-triazoline	>500		Decomposes above 260°C	
5-Phenyltetrazole	472	189	206	214
5-Amino-1H-tetrazole	774		-H_2O, 74°C; Dec. about 220°C	
1,5-Pentamethylenetetrazole	386	149	169	180
1,5-Dimethyltetrazole-1,2,3,4	497	122	139	149
Antioxidant				
4,4'-Thiobis-(3-methyl-6-tert. butylphenol)	-	212	233	243
4,4'-Butylidenebis-(3-methyl-6-tert. butylphenol)	-	210	229	236
6,6'-Di-tert.butyl-4,4'-bis-o-cresol	-	207	220	226
Phenyl-2-naphthylamine	-	175	199	209
Dilauryl thiodipropionate	-	235	256	266
2,6-di-tert. butyl-4-methylphenol	-	92	108	115
5-n-pentadecylresorcinol	-	224	244	252
Di-β-naphthyl-p-phenylenediamine	-		Decomposes above 300°C	

NOTES: 1. In polypropylene containing 0.5% by wt. of 4,4'-thiobis-(3-methyl-6-tert. butylphenol) and 1.5% by wt. of electrolytic grade fine copper dust.

2. Temperatures at which the amounts shown are volatilized in air from the pure compounds in a shallow pan at a constant rise in temperature of 2°C per minute from room temperature. Corrected for loss of water, if observed (*).

TABLE 10. COOPERATION OF COPPER INHIBITORS WITH ANTIOXIDANTS IN POLYPROPYLENE[1] (16)

Copper Inhibitor	Concentration % by wt.	Induction Period at 140°C, Hrs. Antioxidants[2] A	B	C
None, no copper dust	-	961	1040	650
None	-	449	175	133
Oxanilide	0.5	498	436	205
Poly(hexamethylene) oxamide (Nylon 62)	0.5	706	458	190
Maleic acid hydrazide	0.5	-	463	220
Benzhydrazide	0.5	510	266	232
Oxalyldihydrazide	0.1	-	470	-
Oxalyldihydrazide	0.5	-	630	410
Oxalyldihydrazide	1.0	-	960	-
Benzotriazole	0.1	-	639	-
Benzotriazole	0.2	-	600	-
Benzotriazole	0.5	804	605	226
1,3-Diphenyltriazene	0.5	472	432	254
5-Phenyltetrazole	0.5	546	472	286
5-Amino-1H-tetrazole	0.5	598	774	326

NOTES:
1. In polypropylene containing 1.5% by wt. of electrolytic grade fine copper dust.
2. Antioxidant A is N-phenyl-2-naphthylamine.
   Antioxidant B is 4,4'-thiobis-(3-methyl-6-tert. butylphenol).
   Antioxidant C is 6,6'-di-tert. butyl-4,4'-bis-o-cresol.
   The concentration of each antioxidant is 0.5% by wt.

Metal-organic Antioxidant Stabilizers

It has been demonstrated that metal-organic compounds act as oxidation catalysts. Reference 24 also reports on a number of metal-organic compounds which function as highly effective stabilizers for polyolefins. For instance nickel chelate of 2, 2' -thiobis[4 - (1, 1, 3, 3, tetra-methylbutyl) phenol] has been used as a photooxidative and thermal oxidative stabilizer for polyolefins.

A given metal-organic compound exhibits wide range of stabilizing or anti-stabilizing action depending on the chemical nature of its environment, concentration of compound, or any slight change in any or all of these conditions.

An example of a metal-organic antioxidant, zinc (11) dibutyldithiocarbamate for polypropylene is shown in Table 11. Phenolic, aromatic amine, and sulfur-containing antioxidants and a typical synergistic mixture of antioxidants have been included in the table for comparison.

TABLE 11. PERFORMANCE OF ANTIOXIDANTS IN POLYPROPYLENE (24)

Antioxidant[a]	140°C. oven stress-crack life, hr.
None	4
Phenothiazine	15
Dilauryl 3,3'-thiodipropionate	24
4,4'-Butylidenebis [6-tert-butyl-m-cresol]	26
2:1 Ratio dilauryl 3,3'-thiodipropionate:-4,4'-butylidenebis [6-tert-butyl-m-cresol]	96
Zinc (II) dibutyldithiocarbamate	430

[a] Present in 0.1% concentration.

Zinc (II) dibutyldithiocarbamate prolongs the stress-crack life of polypropylene to almost 4.5 times that obtained with the synergistic mixture. However, it is reported that when the total concentrations were increased this ratio decreased. (24)

The synergistic effect of sulfur containing antioxidants on the stability of carbon black pigmented polyethylene has been discussed. Table 12 shows that zinc (11) dibutyldithiocarbamate does not produce this effect despite its sulfur content. This is evidenced by comparing it with an effective synergistic sulfur-containing antioxidant, 4,4' -thiobis (6-tert-butyl-m-cresol).

TABLE 12. PERFORMANCE OF ANTIOXIDANTS IN BLACK POLYETHYLENE (24)

Antioxidant	Antioxidant concn., %	160°C. oven life, hr.
None	-	2
Carbon black (Witco 100)	3	15
Zinc (II) dibutyldithiocarbamate	0.1	>150
4,4'-Thiobis [6-tert-butyl-m-cresol]	0.1	65
Carbon black (Witco 100) Zinc (II) dibutyldithiocarbamate	3 0.1	42
Carbon black (Witco 100) 4,4'-Thiobis [6-tert-butyl-m-cresol]	3 0.1	>150

Table 13 gives the performances of other metal-organic compounds which have been used as polypropylene thermal and photooxidation stabilizers.

TABLE 13. PERFORMANCE OF METAL-ORGANIC COMPOUNDS AS STABILIZERS IN POLYPROPYLENE (24)

Stabilizer[a]	Stress-crack life, hr. of tensile bars	
	140°C. oven	Weather-Ometer
None	9	120
Nickel carbonate	7	170
Nickel (II) stearate	9	190
Magnesium complex of 2,4-pentanedione	12	170
Copper complex of 2,4-pentanedione	5	500
Nickel complex of 2,4-pentanedione	6	650
(Benzoylcyclopentadienyl)cyclopentadienyliron	5	420
(o-Methoxybenzoylcyclopentadienyl)cyclopentadienyliron	5	510
(o-Hydroxybenzoylcyclopentadienyl)cyclopentadienyliron	4	3350
Nickel chelate of 2,2'-thiobis [4-(1,1,3,3-tetramethylbutyl)-phenol]	384	340
Nickel (II) dibutyldithiocarbamate	283	1410
Copper (II) dibutyldithiocarbamate	283	1600

[a] Present in 1% concentration.

[b] Polypropylene contained 0.3 percent of dilauryl 3,3-thiodipropionate and 0.1 percent of 2,6-di-tert-butyl-p-cresol.

The authors of reference 24 report that it is extremely hazardous to predict the performance of stabilizers. For example, the nickel complex 2,4, pentanedione (Table 13) prolonged the stress-crack life of polypropylene by about six. However, the same concentration in polyethylene reduced the stress-life to about one-half that of the unstabilized plastic.

Ultraviolet Stabilizers

The oxidative degradation of polyolefins in air is negligible at low or ambient temperatures. However, exposure to ultraviolet radiation, at low or ambient temperatures, can initiate photooxidation resulting in chain scission, crosslinking and formulation of polar groups.

One of the major problems in developing satisfactory ultraviolet stabilizers is to obtain compatibility with the polymer at rather high levels of concentration and over long exposure periods.

Ultraviolet stabilization is accomplished, generally, by two methods or a combination of these methods with or without antioxidants. The first is by use of absorbing or reactive additives. These additives absorb and dissipate harmlessly the ultraviolet energy directly into the resin. The additive may or may not be opaque in the visible spectrum range.

The additive may stabilize by reacting with the free radicals resulting from the ultraviolet initiated degradation. They also may be employed to stabilize the weak points in an otherwise stable chain by reaction or coordination to prevent the initiation of the degradation reactions. (19)

The second method for inhibiting ultraviolet degradation is by screening the harmful radiation which in polyolefins ranges in the 295-400 millimicron range. This is usually accomplished by the addition of various carbon blacks and pigments.

Since light screeners do let some light pass, combining them with ultraviolet absorbers reduces the amount of degradation reactions which must be handled by the reactive type of stabilizers. Thus a combination of the two methods (often with the synergistic effects of antioxidants) gives adequate protection.

The mechanism by which the photodegradation occurs (i. e., amount of ultraviolet absorption and the rate which the absorbed light initiates free radical reactions) influences the selection of stabilizers (or stabilizer systems).

Also, the thickness of the polyolefin is a deciding factor. Films, for example, will require a higher concentration of stabilizer than a thicker injection molded item for equivalent protection due to its greater surface-to-volume ratio.

Table 14 lists some of the commercially available ultraviolet absorbers. Of the five categories listed, the following general comments can be made: (26)

- Benzophenones - These generally provide extensive protection in the 290 and 380 *u* range while imparting the least color. Usually they can be added in concentrations up to 4 percent without blooming under most molding conditions. The effectiveness depends on the substituted side chains as it increases in length from 2 to 8 carbon atoms.

- Benzotriazoles - These are not as effective as the benzophenones for polyethylene. They are very effective for polypropylene. The substituted hydroxyphenyl benzotriazole absorb ultraviolet in the longer wavelengths 315 - 352 *u*.

- Substituted acrylonitriles - These are primarily used with polyethylene.

- The salicylates - These are rarely used for polyolefins, except in thick and pigmented materials. Although colorless, they impart color and are effective only below 340 *u*. The side chain effect is also evidenced; as you increase the chain from phenyl to tert-butyl to p-octyl the effectiveness increases.

- Metal complexes - Metal chelates are particularly useful for dyed polypropylene. Normally, the metal complexes are used with other ultraviolet stabilizers. They also impart color to the resin and may also develop color after exposure.

TABLE 14. POLYOLEFIN ULTRAVIOLET STABILIZERS

U V Absorber	
Benzophenones 2-hydroxy-4 alkoxy benzophenone 0.1-2.0% (Uvinul 490 Gen. Aniline & Film Corp) 2-hydroxy-4-N-octoxy-benzophenone 0.25-0.5% (Cyasorb-UV531, Am. Cyanamid) 4-dodecyloxy-2-hydroxy-benzophenone 0.25-2.0% (Eastman Inhibitor DOBP, Eastman Chem. Prod) 2, 2' Dihydroxy-4-octoxy BP (Cyasorb UV314, Am. Cyanamid) 2, 2' dihydroxy 4-n-alkoxy benzophenones (UV-287, 313, 314 (Am. Cyanamid) 5-Chloro-2-hydroxy-benzophenone (HCB, Dow) Benzotriazoles Substituted 2, (2'-hydroxy-phenyl) benzotriazone 0.2-0.5%(Tinuvin 327 - Geigy Chem. Corp.) Substituted 2(2'-hydroxy-phenyl) benzotriazole 0.2-0.5%(Tinuvin 326 - Geigy Chem. Corp.) 2(2'-hydroxy-5' methyl phenyl) Salicylates p-octylphenyl salicylate 0.5-1.0%(Eastman Inhibitor OPS, Eastman Chem. Prod. Inc.) 4-t-Butylphenyl salicylate (TBS, Dow) Substituted Acrylonitriles 2-ethyl-hexyl-2 cyano-3, 3-diphenyl acrylate 0.01-5.0% (Uvinul N-539, Gen. Aniline & Film Corp)	Nickel Organic Nickel bisoctyl phenyl sulfide 0.25-0.5% (CI 729) Ferro Corp AM-101 (Ferro Corp) Monobenzoates Resorcinol monobenzoate 1.0-2.0%(Eastman Inhibitor RMB Eastman Chem. Prod. Inc.) Others [2-2'-thiobis(4-t-octyl Phenolato)] -N-butylamine nickel (0.25-0.5% Cyasorb UV1084, Am. Cyanamid Co.) Metal Complexes nickel complex 2, 4-pentanedione Copper complex 2, 4-pentanedione nickel (11) dibutyldithiocarbomate Copper (11) dibutyldithiocarbomate (o-methoxybenzoylcyclopentadienyl) Cyclopentadienyliron (0-Hydroxybenzoyl cyclopentadienyl) Cyclopentadienyliron 2, 2' thiobis (4-t-Octylphenyl) (2.1 nickel complex) Carbon Blacks Channel furnace oil Regal

Table 15 lists some commercially available ultraviolet stabilizers for ethylene-butene copolymers. This data indicates that for the copolymer, the substituted benzophenones are more effective stabilizers than the derivations of phenyl salicylate.

Figure 27 compares the effectiveness obtained in the general class of phenyl salicylate stabilizers by increasing the side chains. Similar curves are shown in Figure 28 for substituted benzophenones. Here the side chain is increased from one carbon atom in UV9 to 8 in UV531.

Illustrations of the significance of stabilized vs unstabilized polyethylene and the influence of stabilization concentration are shown in Figures 29 and 30. (1)

The phenomenon of synergism was explained under antioxidants. Table 16 shows that zinc (11) dibutyldithiocarbamate was poor as an ultraviolet stabilizer in comparison with the benzophenone-type stabilizer. However, the synergistic effect of the two stabilizers is quite evident.

TABLE 15. SOME COMMERCIALLY AVAILABLE UV STABILIZERS (1)

Trade Name	Chemical Structure	Producer	Comparative UV Resistance of Ethylene-Butene Copolymers With Stabilizer[b]	
			Weatherometer Exposure, hr[c]	Tens. Str. and Elong., psi and %[d]
SALOL	Phenyl Salicylate	Dow	375	Brittle
TBS	P-Tertiarybutyl Phenyl Salicylate	Dow	2500	3700 (12)
OPS	P-Octyl Phenyl Salicylate	Eastman	>3000	4100 (13)
BAD[a]	Bis Phenol A Disalicylate	Dow	>3000	4200 (19)
UV-9	2 Hydroxy-4-Methoxy-Benzophenone	American Cyanamid	750	Brittle
UVINUL-40	2 Hydroxy-4-Methoxy-Benzophenone	Antara	-	-
UVINUL-400	2,4-Dihydroxy Benzophenone	Antara	250	Brittle
UVINUL-490	2,2'-Dihydroxy-4,4'Dimethoxy Benzophenone	Antara	250	Brittle
DHPB	2,4-Dihydroxy Benzophenone	Eastman	-	-
HCB	5-Chloro-2 Hydroxy Benzophenone	Dow	250	Brittle
DBR	2,4 Dibenzoyl Resorcinol	Dow	500	Brittle
UV-287	2,2' Dihydroxy-4-Butoxy Benzophenone	American Cyanamid	1000	4100 (11)
UV-314	2,2' Dihydroxy-4 Octoxy Benzophenone	American Cyanamid	>3000	4360 (16)
UV313	2,2' Dihydroxy-Dodecoxy Benzophenone	American Cyanamid	2250	4100 (15)
UV-531	2 Hydroxy-4-Octoxy Benzophenone	American Cyanamid	>3000	4300 (18)
DOBP	4 Dodecyloxy-2 Hydroxy Benzophenone	Eastman	>2000	-
TINUVIN P	2 (2'-Hydroxy-5' Methyl Phenyl) Benzotriazlode	Geigy	625	Brittle
AM-101	Metal-Organic Complex	Ferro-Chemical	750	Brittle

[a] This in an acronym, derived from compound initials. Stabilizer has no trade name.

[b] Ethylene-butene coplymer density of 0.950 gm/cu cm, melt index of 1.2. Stabilizer concentration of 0.5%.

[c] Time required to reduce elongation to less than 10%.

[d] Following 1 yr. exposure in Arizona, elongation values in parentheses.

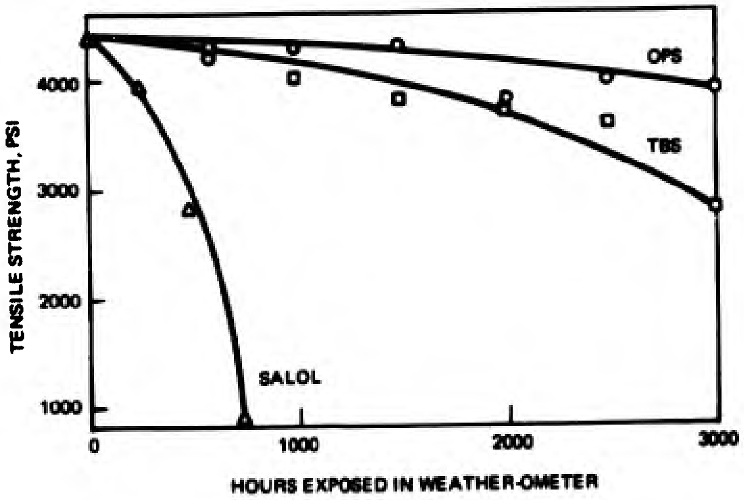


Figure 27. Effect of stabilizer structure for phenyl salicylate derivatives on resistance to UV degradation of ethylene-butene copolymer (1)

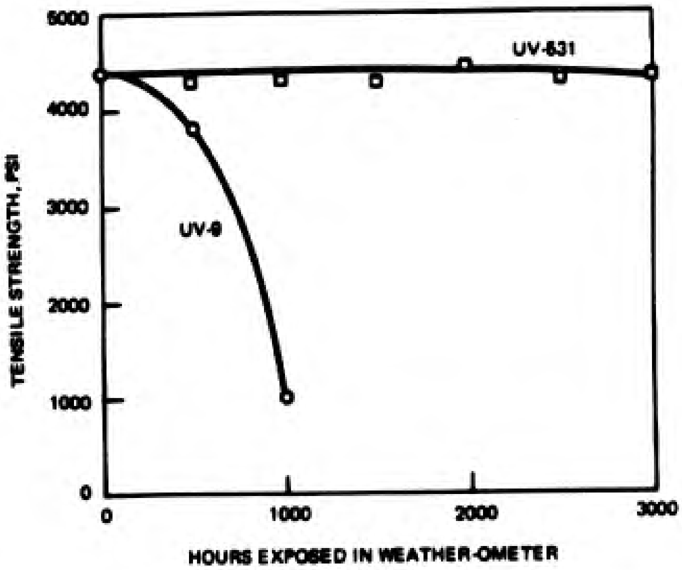


Figure 28. Effect of stabilizer structure of substituted benzophenones (2-hydroxy 4-N-alkoxy-benzophenone) on resistance to UV aging in ethylene-butene copolymer (1)

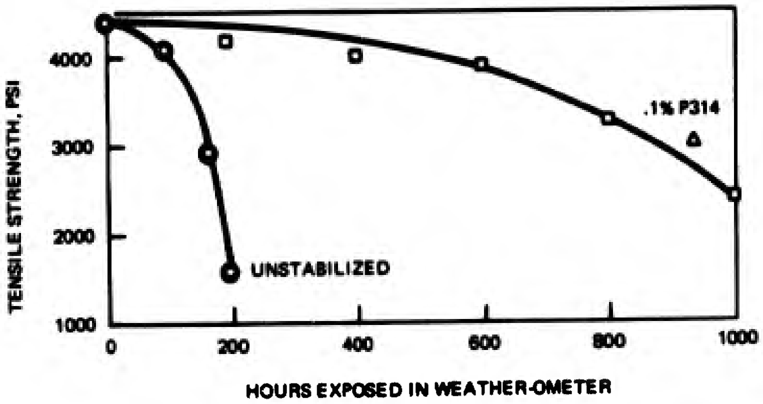


Figure 29. Effect of UV stabilizer on resistance to photodegradation of Marlex .960 density polyethylene (1)

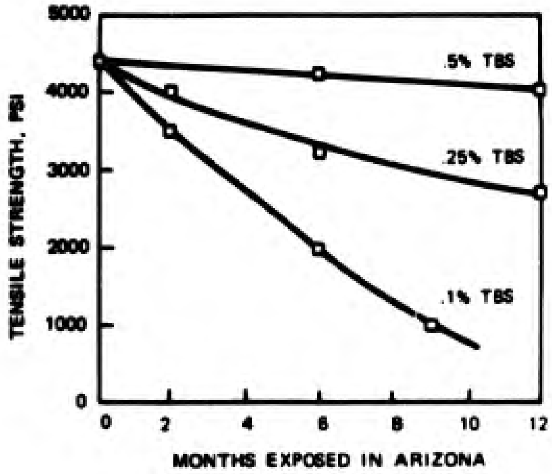


Figure 30. Effect of UV stabilizer concentration on outdoor aging of Marlex .96 density polyethylene (1)

TABLE 16. PERFORMANCE OF ULTRAVIOLET STABILIZERS IN POLYPROPYLENE (24)

Ultraviolet stabilizer	Stabilizer concn., %	Weather-Ometer exposure required for	
		50% loss of initial viscosity, hr.	50% loss of initial elongation, hr.
None	-	200	30
Zinc (II) dibutyldithiocarbamate	3	500	45
2-Hydroxy-4,4'-dimethoxybenzophenone	3	1400	950
{ Zinc (II) dibutyldithiocarbamate	2		
} 2-Hydroxy-4,4'-dimethoxybenzophenone	1	1800	1050

Figures 31 and 32 demonstrate the synergistic effects obtained by combining ultraviolet stabilizers with antioxidants.

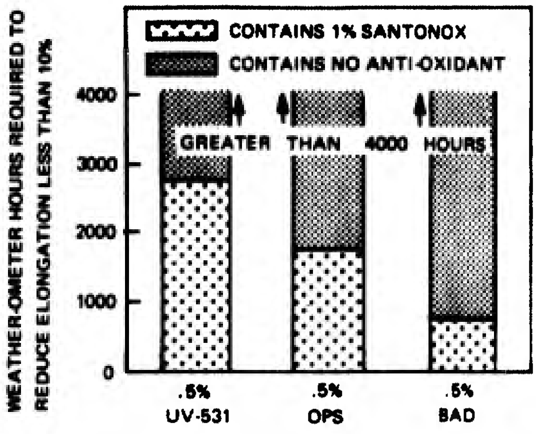


Figure 31. Illustration of the synergistic effect of Santonox with various UV stabilizers in orange pigmented Marlex .96 density polyethylene resin (1)

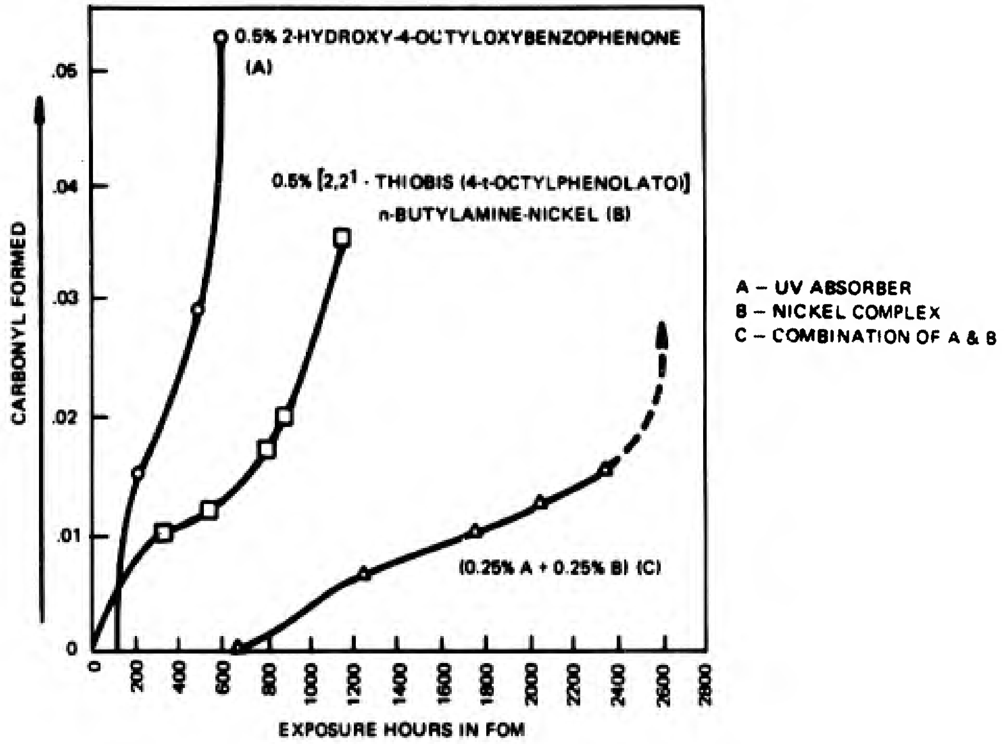


Figure 32. Efficiency of light stabilizers in combination (15 mil polypropylene film) (2)

Carbon blacks

Excellent light stabilization has been obtained in polyolefins by carbon blacks due to their ability to screen light as well as to absorb the entire range of ultraviolet and visible radiation and transform it into less damaging energy.

The types of carbon blacks and factors affecting their efficiency have been covered under antioxidants and generally apply to ultraviolet stabilization. Photo-oxidation of polyolefins is initiated by the radiation energy in the 295 - 330 μ range. The most efficient carbon black particle size for this wavelength is reported to be 10 - 20 μ with small agglomerate sizes in the 70 - 100 μ order. A 2 percent concentration is generally accepted as the quantity for optimum performance.

Figure 33 demonstrates the effectiveness of particle size in deflecting white light from the surface of several carbon black systems.

Table 17 shows the effectiveness of 0.2 phr of carbon black on high density polyethylene exposed in a Fade-Ometer. The smaller percent of carbon black (0.2 instead of 2 percent) was used for accelerating purposes. The results of the first series indicate the best results were obtained with 16 - 29 u particle size, although not universal. The unexpected results with two particle size blacks was attributed to poor dispersion. (23)

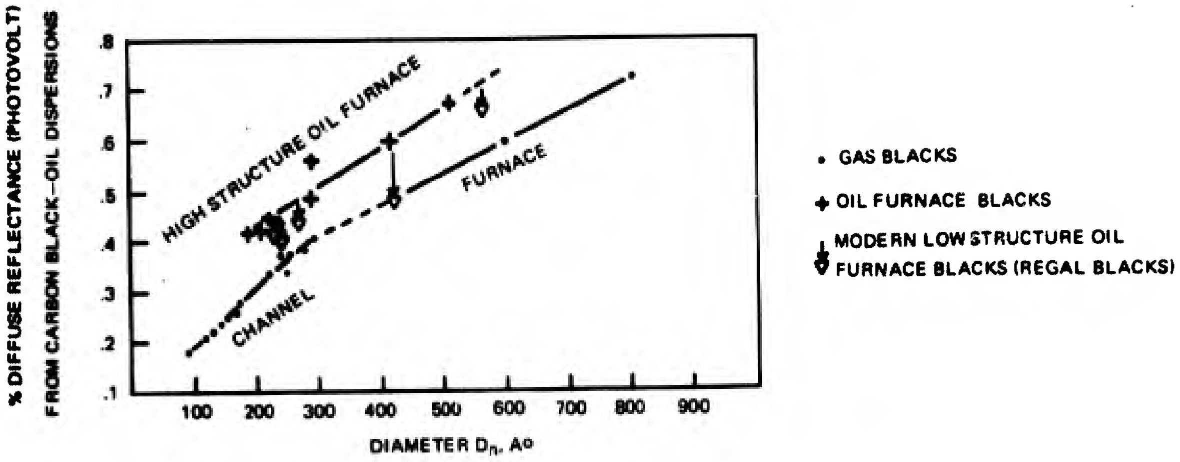


Figure 33. Per cent diffuse reflectance vs. particle size (20)

The main objection to carbon black, of course, is its dark color formulation. This restriction has lead to the development of colorless stabilizers.

In summary, for a stabilizer or stabilizer system to be efficient it must: (26)

- Absorb or screen ultraviolet radiation in the 300 - 400 μ range.
- Provide oxidation protection at the expected exposure temperatures.
- Be compatible with the resin system so not to exude to form a tacky sprew or solid bloom.
- Be compatible with the processing techniques so as not to plate out.
- Have little or no initial color or develop color upon exposure.
- Be relatively inexpensive.
- Be chemically stable (also low toxicity in some applications).
- Be effective for long exposure time.
- Not degrade desirable properties.
- Be extraction resistant to repeated water or solvents.

TABLE 17. LIGHT STABILITY OF HIGH DENSITY POLYTHENE CONTAINING 0.2 PHR CARBON BLACK (23)

	Carbon black	Supplier/Type	Particle Size (milli-microns)	Pigment dispersion rating[b]	Background appearance	Light stability hours irradiation for embrittlement of polymer in carbon arc Fadeometer	Relative light stability[b]
First Run	None	-	-	-	-	135	1.0
	Carbolac 1	CC/ch	9	25	Poor, specky	1550	11.5
	Carbolac 46	CC/ch	13	23/24	Good	1250	9.3
	Columbian 999	CI/ch	13	24	Good	>2000	>14.8
	Rajah	CI/ch	16	23	Good	>2000	>14.8
	Monarch 74	CC/ch	17	23/24	Good	1570	11.6
	Unspecified commercial	-/ch	17	23/24	Good	>2000	>14.8
	Unspecified commercial	-/ch	23	23/24	Good	>2000	>14.8
	Raven 15	CI/ch	25	24/25	Good	>2000	>14.8
	Elf 8	CC/ch	29	23/24	Specky	1750	13.0
	Unspecified commercial	-/ch	29.5	23	Specky	1950	14.5
	Vulcan 3	CC/fu	29	23	Good	>2000	>14.8
	Sterling SO	CC/fu	41	24/25	Coarse	1600	11.9
	Sterling 99R	CC/fu	42	23/24	Specky	800	6.0
Second Run	None	CI/ch	9	22/23	-	230	1.0
	Neo Spectra Mk 11	CC/ch	13	22/23	Specky	3170	23.5
	Carbolac 46[d]	CC/ch	17	22/23	Very good	2300	10.0 c,d.
	Monarch 74[d]	CI/ch	22	22/23	Very good	>3170	>13.8 c,d.
	Peerless Mk. II	CC/ch	25	22/23	Good	2400	17.8
	Elf 0	CI/fu	17	23	Good	2500	18.5
	Statex 16.0 beads	CC/fu	20	23	Specky	>3170	>23.5
	Vulcan 9	CC/fu	21	22/23	Good	1130	8.4
	Vulcan XXX	CC/fu/ch	20	-	Good	2300	17.0
	(50% Sterling 99R + 50% Carbolac 46)	-	-	-	-	27(u)	20.0

[a] .ll samples contain 0.2 phr di-β-naphthyl-ρ-phenylene diamine.

[b] Relative light stability = $\frac{\text{light stability of polymer containing carbon black}}{\text{light stability of polymer}}$

[c] Contains same amount of low density polythene as b. This was used as the reference only for the two materials in which a low density masterbatch was employed.

[d] Carbon black added as a masterbatch in low density polythene of melt flow index 2.

[e] Average particle size calculated from relationship:

$$D \quad \frac{W_1 + W_1}{\frac{W1}{d_1} + \frac{W2}{d_2}}$$

where D = average particle size of blend.
W_1 and W_2 = proportions by weight of the components of the blend.
d_1 and d_2 = corresponding particle size diameters.

CC= Cabot Carbon, Ltd.
CI = Columbian International, Ltd.

Ch = Channel
fu = furnace.

SECTION V. EFFECT OF PIGMENTS ON WEATHER RESISTANCE

The resistance of clear polyolefins to light and ultraviolet radiation has been previously explained, and the chemical reactions which stabilize or sensitize have been described. Many pigments exert similar effects on polyolefin weatherability. In such cases, the weatherability is influenced by the pigment selected, its concentration and particle size, its opacity and ultraviolet absorbing power, and its compatibility with other compounds.

The light resistance of pigments is dependent on their inherent stability to chemical degradation by actinic radiation and their self-screening efficiency (the protection of the bulk of pigment by absorption on the surface layers). Titanium dioxide, cadmium sulfide and selenide, iron oxides and carbon blacks are among the best inherent light resistant inorganic compounds. Chrome yellows usually darken somewhat initially and then endure long exposure without further change. The next best compounds for light resistance are stable organic structures, such as phthalocyanine blues and greens, quinacridone reds and violets, and vat colors. Some benzidine yellows (particularly the HR type) and the manganese BON reds have good light resistance, as does ultramarine blue. (27)

In the metallics and pearlescent colorants, aluminum is unaffected by light but becomes whitened and dulled with moisture. These colorants can even become consumed by corrosive reactions if the water is too acidic (such as ground water) or alkaline. Conventional gold bronzes (brass alloys) are very sensitive to oxidative tarnishing especially in the presence of light, moisture and sulfides. Natural pearlescence (quanine) and synthetic pearl (lead arsenate) are not generally affected by light or exposure to sulfides. Lead carbonate is light resistant but discolors in exposure to hydrogen sulfide. Bismuth oxychloride is quite resistant to sulfide but darkens easily upon exposure to light with its sensitivity extending into the visible range. Therefore, even with ultraviolet absorbers, bismuth oxychloride is not stable for prolonged exposure. (27)

The total quantity, dispersion and mixture of pigments has a decided effect upon color deterioration. Polyolefins with a large quantity of an organic pigment can absorb much radiation and prevent energy concentration at any one pigment site. Also, because of the mass underlying tone, the bleaching effect of the top sacrificial layer is less noticeable. On the other hand, if a small quantity of the same organic pigment is used, the same color loss or bleaching would be very noticeable. It should also be noted that the visible change in color is dependent on the angle or path of light striking the item.

Generally, the following can be said of pigment mixtures:

- Dilute mass tones and tinted mixtures with white are inferior to heavy mass tones. This is due to the increased radiation in the upper layer of plastics from the light reflected and back scattered by the white pigment. Also, the color change is apparent as soon as the pigment overlying the uppermost scattering area is destroyed. In this instance, the undisturbed pigment at the greater depth remains hidden.

- In mixtures of pigments where each has a different individual light resistance, the more ultraviolet resistant pigment may protect the less resistant one.

- In mixtures, if one pigment fades, the resulting change in hue is more noticeable than would be a decrease in intensity of a single color.

- The addition of aluminum to transparent color pigments has a more deterious effect than white. This is due to the concentration of actinic light in the surface layer receiving both direct and reflected rays. Color change is also easily detected against an aluminum background.

- Color pigments mixed with gold bronze perform better since the gold bronze does not reflect strongly in the actinic region.

- Pearlescent pigments do not show the fading of the top layer of the transparent color noticeably because the underlying color can be seen through the pearlescent platelets. However, small quantities of color are normally used with pearlescent pigment which makes them light sensitive.

Figure 34 compares the effectiveness of several pigments to serve as ultraviolet absorbers in compression molded unstabilized high density polyethylene tensile bars.

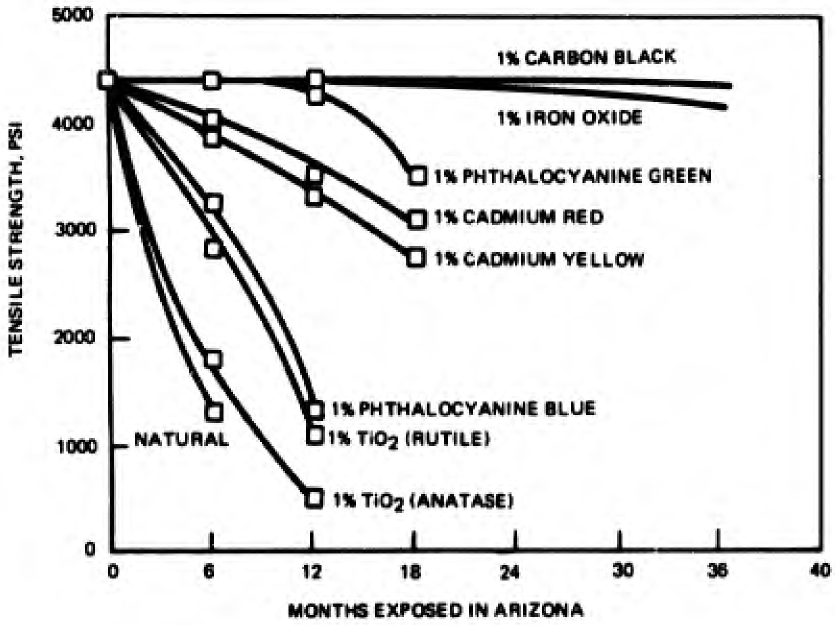


Figure 34. Effect of pigments on UV stabilization of .96 density unstabilized polyethylene resins (1)

Figure 35 shows the effect of 4000 hours exposure in an Atlas Weather-Ometer on high density compression molded tensile bars with 0.5 percent ultraviolet 531, light stabilizer added.

Figure 36 illustrates the effect of pigment concentration on weatherability.

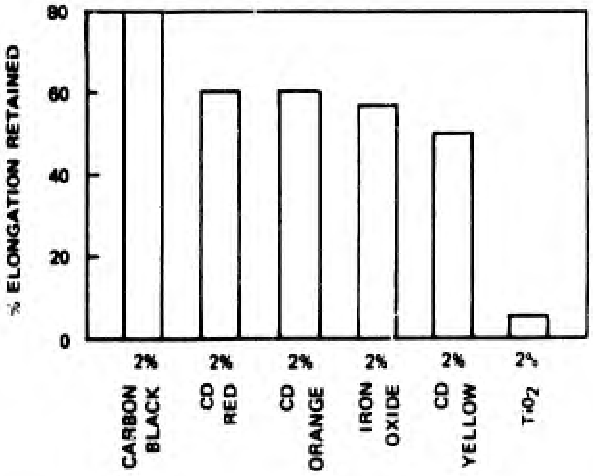


Figure 35. Effect of pigments on UV stabilization of .95 density stabilized polyethylene resins (1)

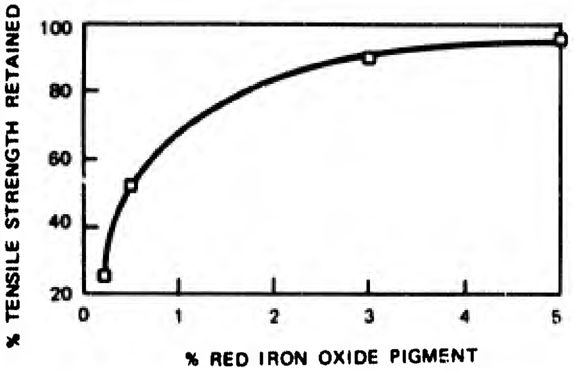


Figure 36. Effect of pigment concentration on outdoor aging of .96 density polyethylene monofilament after one year's exposure in Arizona (1)

Generally, pigments in the blue and violet range give considerably poorer weathering protection to polyolefins than the yellows or oranges. This is due to their ultraviolet transparency and low ultraviolet absorption. This would also mean that among the white pigments anatase titanium dioxide, which has the purest blue-white hue, is less effective than the rutile type pigment. (27)

Although titanium dioxide is a light resistant pigment, incorporation of large amounts in polyolefins can actually accelerate deterioration. (Figure 37) This is due to the increased intensity of radiation on the surface layer from the light reflected and back scattered by the white pigment.

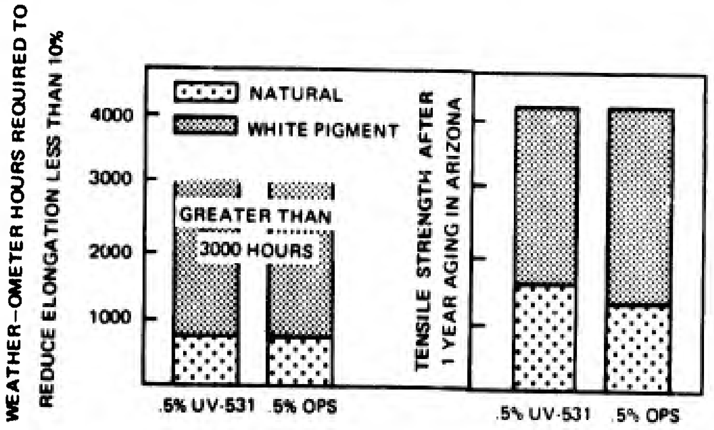


Figure 37. Effect of titanium dioxide pigment on weathering performance of .96 density polyethylene (1)

The reflective pigments (metallics and pearlescents) in addition to their natural chemical reactions, create stability problems because they are normally used in a clear compound for optimum brilliancy.

The advantages of adding ultraviolet absorbers to pigments depends on the wave lengths which the pigment transmits or is affected by. Pigments which in themselves are strong ultraviolet absorbers or are sensitive to visible radiation do not benefit much from the addition of ultraviolet absorbers.

There is also a problem of compatibility of compounds with polyolefins. For example, when large amounts of ultraviolet absorbers are used to protect sensitive pigments, blooming or exudation occurs with all but the most non-polar ultraviolet compounds. Polypropylene is not as sensitive to this problem. (27)

SECTION VI. POLYOLEFIN WEATHERING DATA

Figure 38 shows the effect of density, melt index and pigmentation on the weathering of polyethylene bent strips. Ten 1.5" x 0.5" x 0.125" specimens were cut from compression molded plaques. A 0.020" deep longitudinal slit was cut into the center of each specimen. The specimens were then bent into a "U" shape with a stress inducing slit on the outside and inserted into a channel. Exposure was at Southeast Texas and Western Pennsylvania.

The time for 50 percent failure is shown in the figure. A failure is defined as a crack or hole which later forms a crack in the stressed area.

The effect of melt index is quite evident. For example, comparing the copolymers 6515 and 6530, a three- to five-fold increase in life was obtained by using a lower melt index. Also, a two- to three-fold acceleration was obtained by varying the exposure to a more southerly environment.

The 0.96 density 0.5 melt index homopolymers failed in 8 to 9 weeks. The yellow and black pigment gave little protection in this formulation. It is interesting to note that the natural high density polyethylene with a 0.25 melt index weathered 10 weeks but when cadmium yellow pigment was added, its life was extended to 111 weeks or over two years. (6)

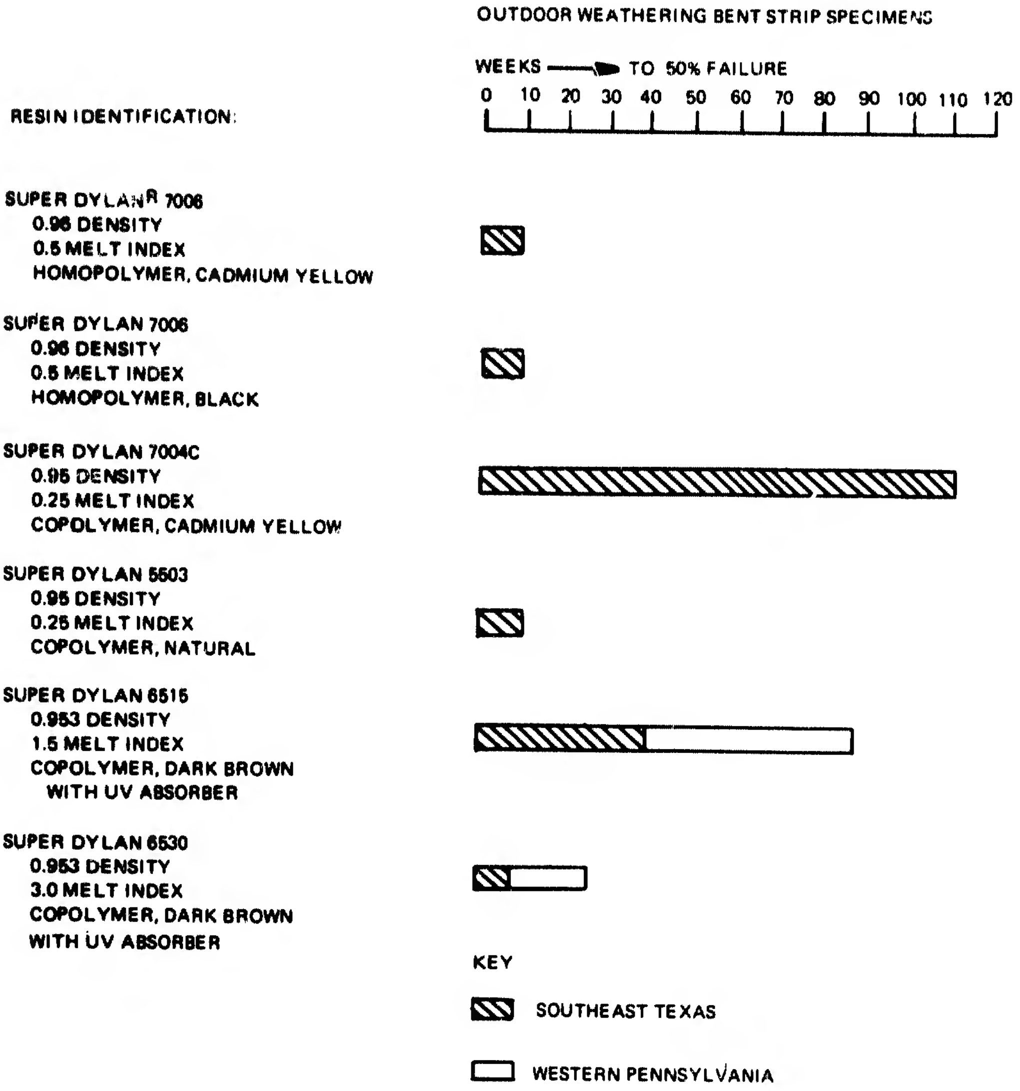


Figure 38. Effect of density, melt index, and pigmentation on polyethylene weatherability (6)

Polyolefin compositions were exposed under stress to accelerate the evaluation of ultraviolet stabilizers and to measure the minimum useful lifetime of the compositions. (28)

Specimens 1 1/2" long by 1/2" wide were cut from a compression molded plate 1/8" thick and bent into a "U" shape and inserted upside down in a channel 1/2" wide and 3/8" deep. Ten specimens of each formulation were exposed at 36 1/2° with the horizontal facing south at Kingsport, Tennessee. The data in Table 18 give the exposure time required to crack the first, fifth, and tenth specimens as well as to break the first specimen. The exposure time is given in milliequivalents of oxalic acid decomposed in an uranyl oxalate actinometer. This was done to smooth out seasonal variations in actinic radiation intensity.

Most formulations had small variations in time to crack between the first and tenth specimens. Larger variations occurred in time to break after the first specimen cracked. This varied from two months for the copper complex with α, α^1-(ethylenedinitrilo)di-*o*-cresol to seven years for the 2, 4-dihydroxybenzophenone.

TABLE 18. STRESS CRACKING OF LOW-DENSITY POLYETHYLENE[(a)] AT KINGSPORT, TENNESSEE (28)

Additive	Exposure, Meq.[(b)]				
	Amt., Parts Per 100 Parts Polyethylene	1st Specimen to Crack	5th Specimen to Crack	10th Specimen to Crack	1st Specimen to Break
None	-	46	46	48	102
Copper complex with α, α'-(ethylenedinitrilo)di-*o*-cresol	1	24	24	28	37
Titanium (IV) oxide (rutile)	5	42	48	50	64
Iron (III) oxide (Mapico Red 297)	5	50	50	55	390
2,4-Dihydroxybenzophenone	1	61	70	84	416
Dilauryl 3,3'-thiodipropionate	0.5	64	75	102	374

(a) Tenite Polyethylene 800.

(b) Milliequivalents of oxalic acid decomposed in an uranyl oxalate actinometer. Approximately 50 meq. of oxalic acid are decomposed in an actinometer in one year.

A correlation between stress-cracking and loss of elongation was also made. The results are given in Table 19 by means of a stabilization rating.

The stabilization rating ranged from 0. 5 (copper complex with α, α^1-(ethylenedinitrilo) di-*o*-cresol) to greater than 10. 5 for 4-(Dodecyloxy)-2-hydroxybenzophenone and carbon black. Since the "greater than" symbol is only used to indicate the extent of exposure to date, it should not be inferred that the colorless stabilizer 4-(Dodecyloxy)-2-hydroxybenzophenone is as effective as carbon black.

TABLE 19. CORRELATION OF STRESS CRACKING OF LOW-DENSITY POLYETHYLENE (a) WITH LOSS IN ELONGATION DURING OUTDOOR WEATHERING (28)

Additive	Amt., Parts Per 100 Parts Polyethylene	Stress Cracking$^{(b)}$		Elongation$^{(c)}$	
		Stress-Crack Life, Meq.$^{(d)}$	Stabilization Rating$^{(e)}$	Exposure Required to Reduce Elongation to 100%, Meq.$^{(d)}$	Stabilization Rating$^{(e)}$
None	-	46	1.0	45	1.0
Copper complex with α, α'-(ethylenedinitrilo)di-o-cresol	1	24	0.5	28	0.6
Resorcinol monobenzoate (Eastman^{R} Inhibitor RMB)	1	66	1.4	85	1.9
2,4-Dihydroxybenzophenone	1	70	1.5	96	2.1
Dilauryl 3,3'-thiodipropionate	0.5	75	1.6	62	1.4
Phenyl salicylate (Salol)	1	94	2.0	46	1.0
2-Hydroxy-4-methoxybenzophenone (Cyasorb 9, American Cyanamid Co.)	1	129	2.8	100	2.3
p-tert-Butylphenyl salicylate (TBS, Dow Chemical Co.)	1	182	4.0	70	1.5
o-Octylphenyl salicylate	1	>427	>9.3	>260	>5.8
4-(Dodecyloxy)-2-hydroxybenzophenone (Eastman^{R} Inhibitor DOBP)	1	>483	>10.5	>300	>6.7
Carbon black (Black Pearls 71)	3	>483	>10.5	-	-

(a) Tenite Polyethylene 800.

(b) 1/8-In.-thick specimen.

(c) 1/16" thick, 2-1/2" long and 1/2" wide specimen. Gage section was 1" long and 1/4' wide. Elongation rate was 2000% min.

(d) Milliequivalents of oxalic acid decomposed.

(e) Stabilization rating = $\frac{\text{Exposure time for failure of stabilized composition}}{\text{Exposure time for failure of unstabilized composition}}$

The greater effectiveness of the phenyl salicylate and p-tert-butylphenyl salicylate in the 1/8" thick specimens over the 1/16" thick specimens was attributed to the more rapid volatilization from the thinner specimens. Considering the difference in thickness, the two test methods correlated rather well. (28)

A comparison of Weather-Ometer stress-crack life with outdoor stress-cracking at Kingsport, Tennessee is given in Table 20.

The Weather-Ometer used was an Atlas Twin-Arc, type DLTS, modified with ten Westinghouse fluorescent sunlamps and an air-water fog nozzle to increase the relative humidity. The machine was operated at a black panel temperature of 145°C and a relative humidity of 50 percent. One 24-minute water spray cycle per each 24 hours of operation was used. (28) The specimens were mounted with the same stress as those exposed outdoors. However, only three specimens were exposed and the results are the average exposure time in hours, to develop cracks in all three specimens.

The data show the Weather-Ometer and outdoor exposure correlate as follows: three compositons were within 20 milliequivalents of oxalic acid or one summer's exposure; four compositions underestimated the outdoor exposure and the remaining formulations overestimated the outdoor exposure. This latter effect was attributed to the overemphasis of antioxidants and is noticeable with the formulation concerning 2, 2'-methylenebis (6-tert-butyl-p-cresol).

TABLE 20. CORRELATION OF LOW-DENSITY POLYETHYLENE (a) STRESS CRACKING IN A MODIFIED WEATHER-OMETER WITH STRESS CRACKING OUTDOORS AT KINGSPORT, TENNESSEE (28)

Additive	Amt., Parts Per 100 Parts Polyethylene	Stress-Crack Life		
		Weather-Ometer, Hr.	Outdoors, Meq. (b)	Predicted Outdoor Life, Meq. (b)(c)
None	-	450	46	-
2,2'-Dihydroxy-4-methoxybenzophenone	1	1,750	50	151
Lead chromate (VI) (Chrome Yellow M)	5	640	54	63
Nickel complex with 2,4-pentanedione	1	240	59	23
2,4-Dihydroxybenzophenone	1	2,080	70	202
Dilauryl 3,3'-thiodipropionate	0.5	800	75	78
Dibenzoylresorcinol (Dow Stabilizer DBR)	1	1,350	153	138
2-Hydroxy-4-methoxybenzophenone	1	700	154	68
2-(2H-Benzotriazol-2-yl)-p-cresol	1	450	161	44
Lead chromate (VI) (Chrome Yellow M) 2,2'-Methylenebis [6-tert-butyl-p-cresol] (Antioxidant 2246)	5 0.5	6,900	308	673
Phenyl 3-phenylsalicylate	1	5,840	376	571
4-(Dodecyloxy)-2-hydroxybenzophenone	1	2,610	>483	255
Carbon black (Black Pearls 71)	3	22,000	>483	2,150

(a) Tenite Polyethylene 800.

(b) Milliequivalents of oxalic acid decomposed.

(c) Based on unstabilized polyethylene, 450 hr. in Weather-Ometer equals the stress-cracking outdoors where 46 meq. of oxalic acid was decomposed.

Injection-molded polypropylene tensile specimens 2 1/2" long were stressed in a 5/8" wide channel similar to the polyethylenes. Three specimens of each formulation were examined for stress cracking in both the Weather-Ometer and outdoors. The results are given in Table 21.

TABLE 21. ULTRAVIOLET STRESS CRACKING OF POLYPROPYLENE [(a)] (28)

Additive (1% Concn.)	Stress-Crack Life		
	Modified Weather-Ometer, Hr.	Outdoors, Meq.[(b)]	Predicted Outdoor Life, Meq.[(b)(c)]
None	140	24	-
Nickel complex with 2,2'-thiobis [4-(1,1,3,3-tetramethylbutyl)phenol]	330	40	55
Nickel complex with 2,4-pentanedione	520	43	87
4-Methoxy-2-hydroxybenzophenone	420	55	70
p-(1,1,3,3-Tetramethylbutyl)phenyl salicylate (Eastman^{R} Inhibitor OPS)	1,220	57	204
4-(Octadecyloxy)-2-hydroxybenzophenone	490	62	82
4-(Octyloxy)-2-hydroxybenzophenone	1,015	105	174
4-(Dodecyloxy)-2-hydroxybenzophenone (Eastman^{R} Inhibitor DOBP)	1,750	108	292
1:1 Mixture of 4-(dodecyloxy)-2-hydroxybenzophenone and nickel complex with 2,4-pentanedione	2,520	160	430

(a) Tenite Polypropylene 4230.

(b) Milliequivalents of oxalic acid decomposed.

(c) Based on unstabilized polypropylene, 140 hr. equals 24 meq. of oxalic acid decomposed.

The data are arranged in order of increasing outdoor stability and indicate that all Weather-Ometer predictions were higher than the outdoor lifetime measured. Although not shown, larger variations among the cracking times of the polypropylene specimens versus the polyethylene was reported. (28)

Figure 39 compares the effect of various light sources upon polypropylene film embrittlement with two different light stabilizers. The film was considered brittle when it could not be folded 180° without cracking. (2)

The same test was repeated in Figure 40 but with an antioxidant added to the formulations. The data show that the protection of light stabilizers varies considerably under different artifical sources and outdoor exposure. It also illustrates the significance of combining an antioxidant with ultraviolet stabilizers.

Additional data on the effects of ultraviolet stabilizers with and without antioxidants is given in Table 22 and Figure 41 for polypropylene and Tables 23 - 26 for polyethylenes.

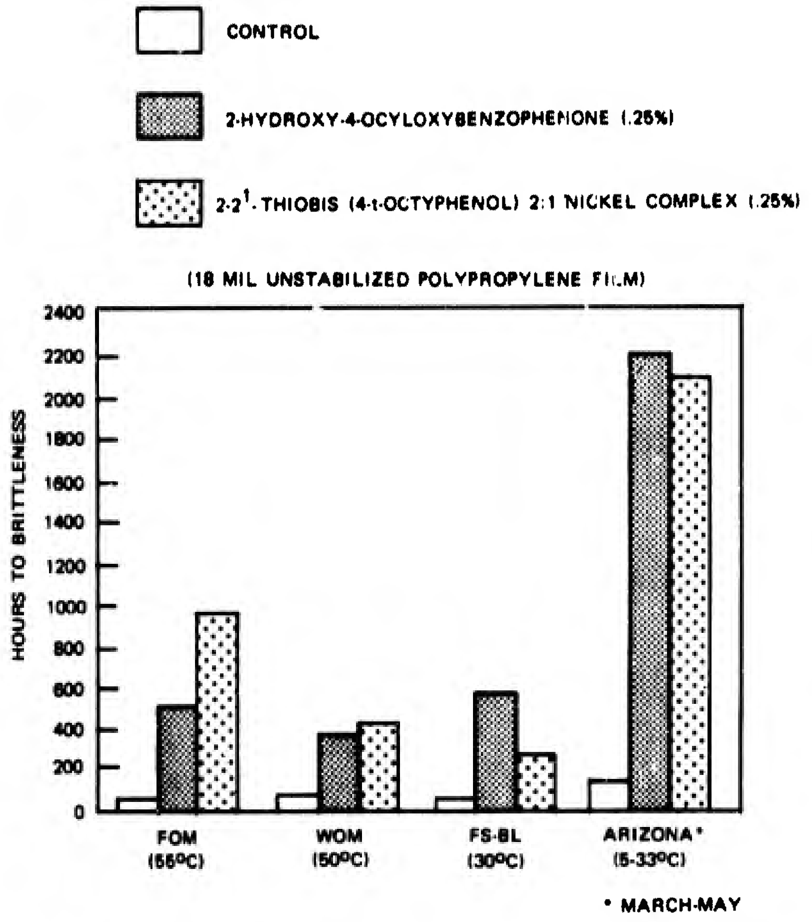


Figure 39. Effect of light source upon polymer embrittlement (2)

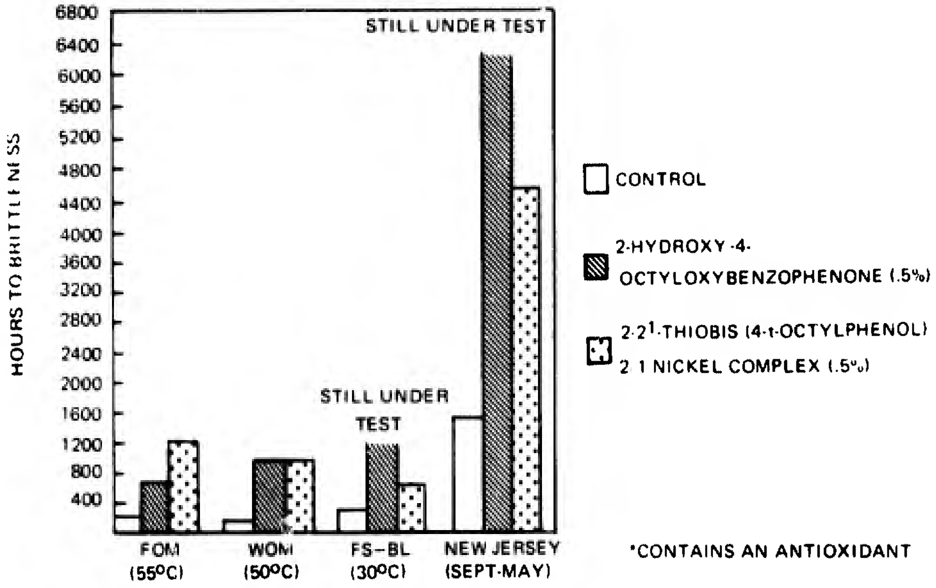


Figure 40. Effect of light source upon polymer embrittlement (14 mil commercial polypropylene film*) (2)

TABLE 22. RESISTANCE OF 1/16 IN. POLYPROPYLENE TENSILE BARS TO OUTDOOR WEATHERING[(a)] (30)

Treatment	Exposure Time in Months, Required for:			
	Stress Cracking[(b)]	Stress Crack life[(b)(c)]	50% loss of Initial Elongation	90% loss of Initial Elongation
Control	0.8	-	0.7	0.7
1.0% Eastman Inhibitor DOBP				
Control[(d)]	-	2	-	-
1.8% Eastman Inhibitor DOBP[(d)]		>15		

(a) Kingsport, Tennessee
(b) Specimens, 1-1/2 in. x 1/2 in., mounted under stress
(c) time for 50% of specimens to crack
(d) Contains 0.1% 2,6-di-tert-butyl-p-cresol and 0.1% dilauryl thiodipropionate

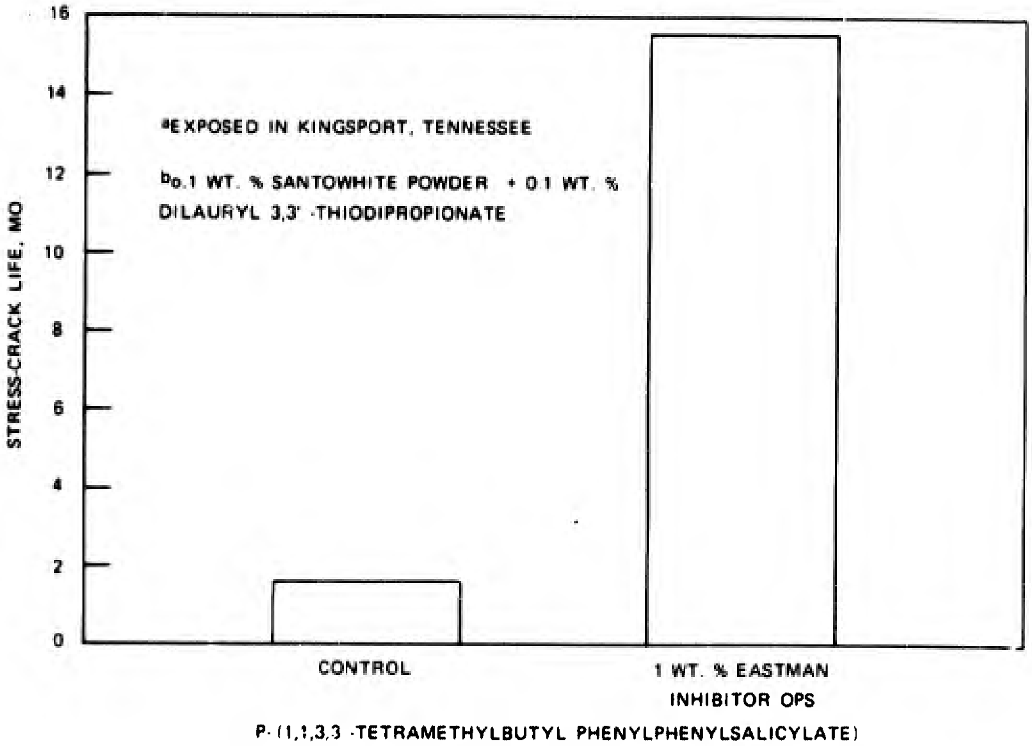


Figure 41. Resistance to outdoor weathering[a] of 0.063-in. (1.6mm.) polypropylene[b] (29)

TABLE 23. EFFECTIVENESS OF ULTRAVIOLET INHIBITORS IN LOW DENSITY (0.92) POLYETHYLENE AFTER OUTDOOR WEATHERING IN KINGSPORT, TENNESSEE (29)

Stabilizer	% Original Elongation Retained[a]		Carbonyl Formation[b]		Exposure Time Required To Crack One-Half of 10 Bent Samples[c], Mo.
	After 1 yr.	After 2 yr.	After 3 mo.	After 1 yr.	
None	9	2	35	100	12
1 wt. % Phenyl Salicylate	13	9	9	24	22
1 wt. % EASTMAN Inhibitor OPS	80	53	1	14	56

[a] Determined on 50-mil or -thou (1.3-mm.) molded plate

[b] Determined on 50-mil or -thou (1.3-mm.) molded plate. Carbonyl formation is expressed in arbitrary units of infrared absorption.

[c] Determined on 0.125-in (3.2-mm.) molded plate.

TABLE 24. EFFECT OF OUTDOOR WEATHERING(a) ON 125-MIL STRESSED POLYETHYLENE PLATES (30)

Sample	Exudation	Outdoor Stress-Crack Life, Months
Control	None	12
1% Eastman Inhibitor DOBP	None (outdoors)	84
2,4-Dihydroxybenzophenone	Heavy	15

(a) Exposed at Kingsport, Tennessee

TABLE 25. EFFECT OF OUTDOOR WEATHERING(a) ON 50-MIL POLYETHYLENE PLATES(b) (30)

Sample	Per Cent Original Elongation Retained After			Carbonyl Formation After (in arbitrary absorption units at 5.82μ)				
	1 yr.	2 yr.	3 yr.	3 mo.	1 yr.	2 yr.	3 yr.	5 yr.
Control	9	2	-	35	ca. 100	-	-	-
1% Eastman Inhibitor DOBP	-	-	-	3	4	12	20	32
1% Eastman Inhibitor DOBP + 0.5% dilauryl 3,3-thiodipropionate	110	85	88	3	5	7	9	12
0.5% Dilauryl 3,3-thiodipropionate	-	-	-	20	>40	-	-	-

(a) Exposed at Kingsport, Tennessee

(b) TENITE Polyethylene 800, density -0.9

TABLE 26. LIFE EXPECTANCY OF UV STABILIZED .96 DENSITY POLYETHYLENE (14)

Formulation	Stabilizer	Life, months		
		Florida	Arizona	New Jersey
0.7 melt Index, comp. molded, .07" thick	None	6	3	12
0.2 melt Index Extrusion, 0.05" thick	0.25 TBS	11-16	10	28*
3.5 melt Index comp. molded .07" thick	0.5 TBS	-	12+	-
0.2 melt Index comp. molded .06" thick	0.5 UV-531	16	12+	36

Stabilizers (UV): TBS - p-tert. butyl phenyl salicylate
UV-531 - 2-hydroxy, 4-octoxy benzophenone

End-point: Manual bend, or 10% of tensile elongation retained, or 2/3 of tensile strength retained. Plus (+) indicates that end-point not reached when test stopped.

*Extrapolated from elongations at 3, 6, 9 and 12 months

The effect of specimen thickness on polyethylene weathering is demonstrated in Figures 42, 43 and 44. Figure 42 compares the elongation at fracture of unstabilized and inhibited polyethylene of various thicknesses. The elongation-at-fracture data give the condition of the film sample up to the time of failure of the area in contact with the wooden mounts. When this area failed the specimens were lost and tests ended. Therefore, the lengths of the elongation curves show the approximate failure time of the film adjacent to the mounts; the heights of the curves show the condition of the general area. (31)

The samples in Figure 42 were to be removed after 4 months; however, the 1 mil film was missing before the 4month period. The 5 mil film was lost between 8 and 12 months; the 10 mil film was lost between 12 and 18 months. The 20 mil sample lasted 18 months but was lost before 24 months.

The 1 mil stabilized film was lost after 18 months; the 5 mil between 24 and 36 months. The 10 and 20 mil stabilized film were still under test after 43 months.

The difference in film elongations prior to weathering was attributed to differences in the orientation produced during manufacture.

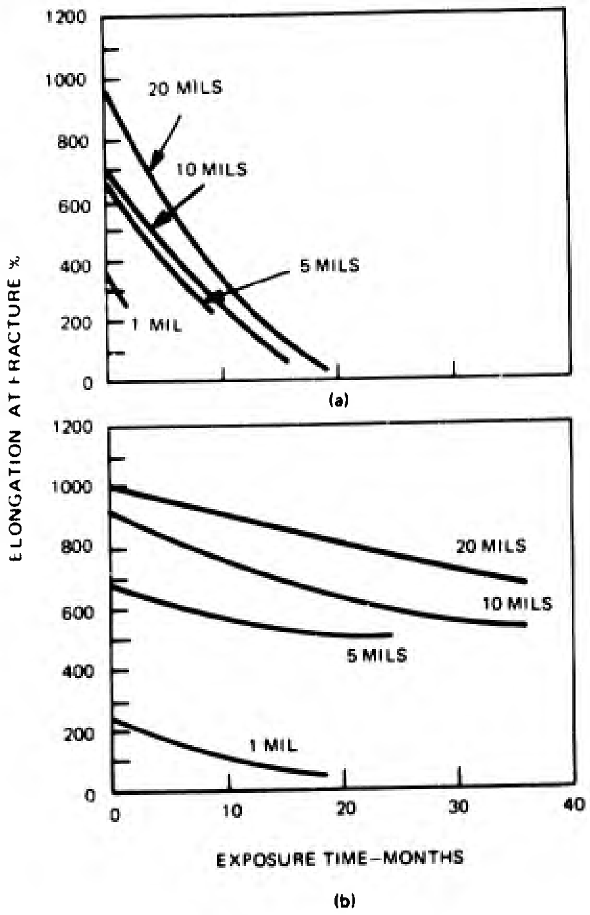


Figure 42. Weathering of uninhibited and stabilized (UV 1 - No. 50) Tenite polyethylene plastic film (31)

Note
- a - Uninhibited
- b - Contains UV 1 - No. 5 stabilizer

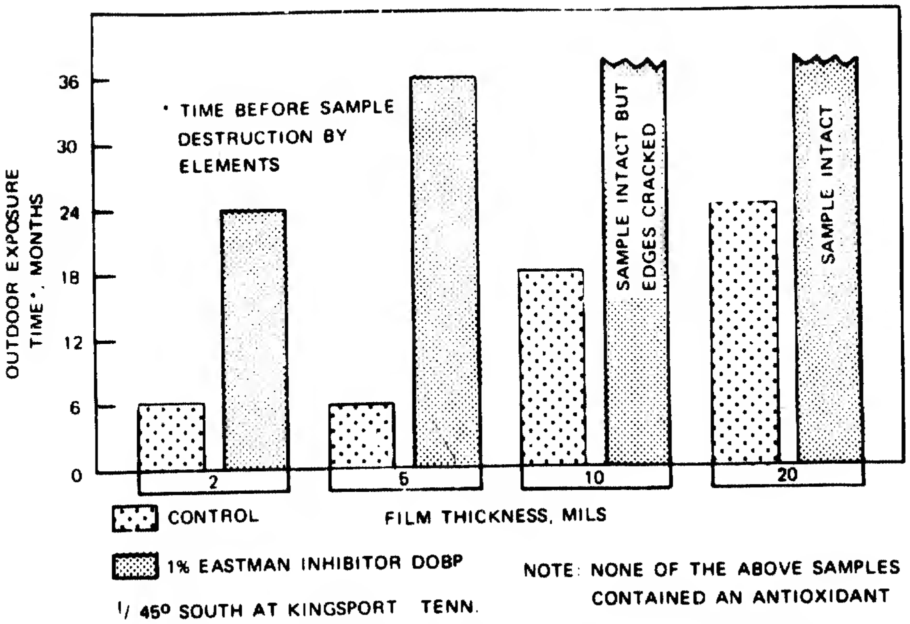
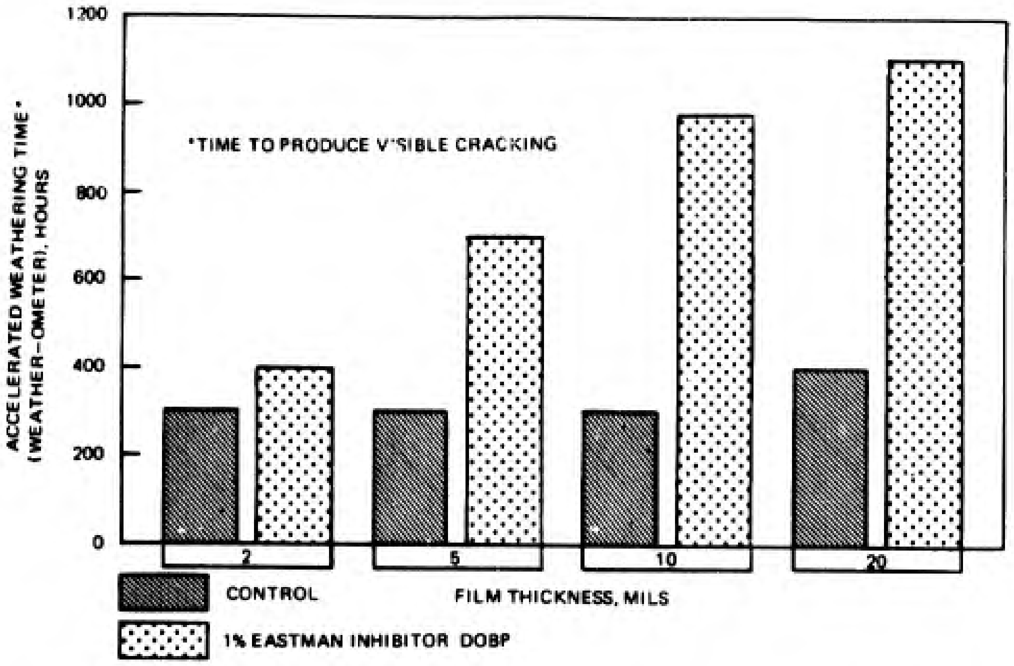


Figure 43. Outdoor weathering life of films made of low density (0.9) Tenite polyethylene 860 stabilized with Eastman Inhibitor DOBP (30)



NOTE: NONE OF THE ABOVE SAMPLES CONTAINED AN ANTIOXIDANT

Figure 44. Accelerated weathering life of low density (0.9) Tenite polyethylene 860 stabilized with Eastman Inhibitor DOBP (30)

Tables 27 -29 and Figures 45 and 46 illustrate the effect of ultraviolet stabilizer concentration on weatherability.

TABLE 27. TYPICAL WEATHERING DATA OF BRANCHED AND LINEAR POLYETHYLENE (32)

%Elongation vs. Hours of Accelerated Weathering*						
Ferro AM-101[1]	- Branched Polyethylene			- Linear Polyethylene		
	Hours of Exposure			Hours of Exposure		
Concentration, %	0	150	250	0	150	250
0.0 (unmilled sample)	545	105	26	-	-	-
0.0 (milled sample)**	388	86	0	273	40	3
0.2	400	366	175	425	70	7
0.5	262	247	252	445	180	85

[1] Ferro AM-101 is a metal-organic UV stabilizer.

* - Accelerated weathering was conducted in a Fade-O-Meter. 5 mil, extruded film was used for testing.

** - The standard procedure includes a 10 minute milling of the resin and additive, at or near the melt temperature of the respective resins, on a 2-roll plastics mill, to insure complete dispersion.

TABLE 28. WEATHER-OMETER[a] EXPOSURE OF LOW-DENSITY (0.92) POLYETHYLENE [50-mil or -thou (1.3-mm.) films] (29)

Inhibitor	Exposure Time Required to Cause 50% Loss in Elongation, Hr.	Exposure Time for the Formation of 15 Arbitrary Carbonyl Units, Hr.
Control	180	110
0.6 wt. % EASTMAN Inhibitor OPS	670	640
1.0 wt. % EASTMAN Inhibitor OPS	810	600

[a] Atlas Weather-Ometer, Modified DLTS.

TABLE 29. WEATHERING RESISTANCE OF 3-MIL CAST FILM OF POLYPROPYLENE (30)

Treatment	Accelerated Weathering(a) Stabilization Rating (Based on Embrittlement)	Outdoor Weathering(b) Exposure Time, in Weeks, to Cause Embrittlement
Control	1	5
1% Eastman Inhibitor DOBP	3	-
2% Eastman Inhibitor DOBP	9	-
5% Eastman Inhibitor DOBP	23	33
3.3% Eastman Inhibitor DOBP + 1.7% Dilauryl 3, 3'-thiodipropionate	-	66

(a) Modified DLTS Weather-Ometer

(b) Exposed in Kingsport, Tennessee

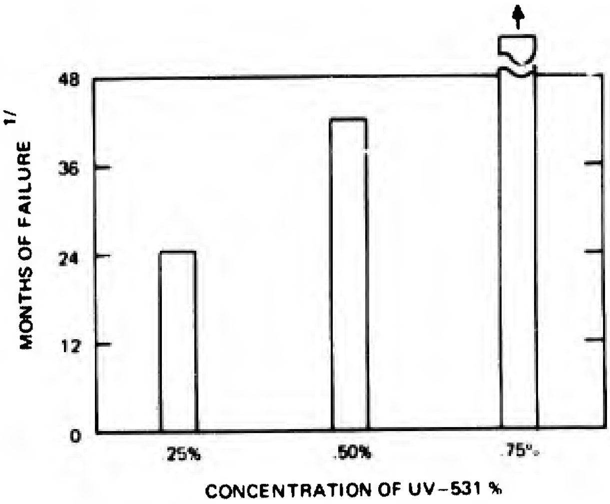


Figure 45. Exposure of 3 levels of UV-531 in high density polyethylene at 45° south (Arizona) (12)

1) Failure point at which tensile strength is 2/3 of original strength

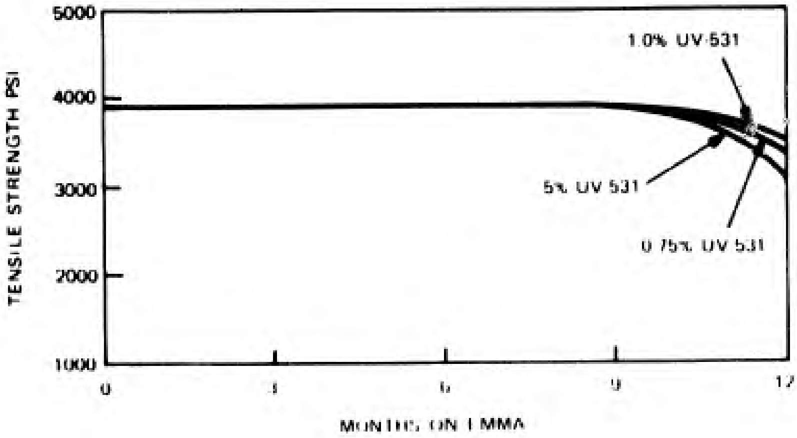


Figure 46. Effect of UV concentration on weatherability of high density polyethylene exposed on EMMA (12)

Figure 47 shows the stabilizing effects of two types of carbon blacks on ethylene-butene-1 copolymer blends exposed in EMMA in Arizona. Although the tensile strengths were virtually unchanged, the elongation of the channel black and furnace black specimens were reduced by 37 percent and 16 percent, respectively. It should be noted that this data applied to EMMA exposure and does not agree with specimens containing 2 1/2 percent furnace black exposed 25,000 hours in an Atlas Weather-Ometer where no significant brittleness occurred. (12)

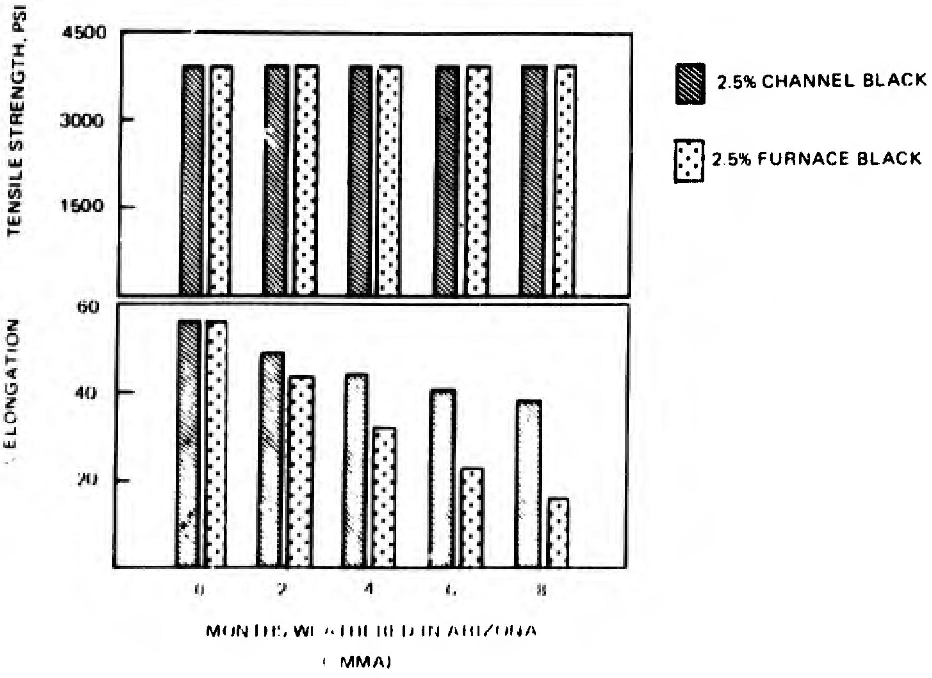


Figure 47. Effect of carbon black type on weathering of Marlex ethylene-butene-1 copolymer (12)

The weatherability of ASTM round-robin polyethylene compositions with varying carbon black dispersions is assessed by various means in Table 30. (33)

TABLE 30. WEATHERING RESISTANCE OF ASTM ROUND-ROBIN POLYETHYLENE COMPOSITIONS CONTAINING VARIOUS CARBON BLACK DISPERSIONS (33)

RR No.	Type of carbon black	Microscope dispersion rating: 100X	Optical absorptivity (white light: film thickness, 1 mil)	Weatherability (1)			
				3-mil films		1/16-in. tensile specimens (2)	1/8-in. stressed strips (3)
				Original elongation retained after: 375 hr. in Weather-ometer	3 yr. outdoors	Original elongation retained after 7 yr. outdoors	Surface cracking after 8.5 yr. outdoors
			cm.^{2}/g.	%	%	%	-
1	Channel, fine	Good	45,000	88	40	90	None
2	Furnace, fine	Fair	49,000	68	80	80	None
3	Acetylene	Good	33,000	55	13	77	None
4	Furnace, coarse	Fair	32,000	57	21	76	None
5	Lamp-black	Good	28,000	51	15	81	None
6	Channel, coarse	Fair to poor	46,000	82	45	82	None
7	Channel, fine	Fair	45,000	64	26	93	None
8	Channel, fine	Poor	44,000	69	29	94	None
9	Furnace, fine	Very poor	31,000	41	6	93	Very slight
10	Lamp-black	Very poor	22,000	25	1	49	Severe[a]
Control	None	--	0	0	0	0	Broken[b]

a--Cracks first visible after 1.5 yr. exposure.
b--Cracks first visible after 1 yr. exposure. Samples broken after 2 years.
1) Kingsport, Tenn.
2) compression molded
3) 1-1/2 x 1/8" x 1/2" [illegible]ression strips in 1/2" wide shape channels.

Table 31 presents the effect of three years outdoor weathering on the electrical and mechanical properties of two polyethylene formulations at three sites. The exposure at each site was 45° facing south. Although carbon black reduces the electrical properties of polyethylene to the extent that they cannot be used for primary insulation, they can be used for cable jacketing, etc. The poorer electrical properties of the electrical versus the pipe formulation was attributed to glomerates of carbon black in isolated areas rather than to the increase in amount of carbon black. (34)

TABLE 31. EFFECT OF OUTDOOR WEATHERING ON ELECTRICAL AND MECHANICAL PROPERTIES OF POLYETHYLENE (34)

		Valves (1)								
Exposure:	Control	Arizona			Florida			Michigan		
Time, yrs:	0	1	2	3	1	2	3	1	2	3
Polyethylene, Electrical formulation(2):										
Dielectric constant:										
At 10^6 cps	2.9	3.5	3.6	4.0	3.5	3.5	4.0	3.0	3.1	4.4
At 5×10^7 cps	--	--	--	3.2	--	--	3.2	--	--	*
Dissipation factor:										
At 10^6 cps	0.012	0.050	0.040	0.065	0.030	0.030	0.060	0.020	0.020	0.090
At 5×10^7 cps	--	--	--	0.012	--	--	0.120	--	--	*
Tensile strength, psi	1800	1650	1850	1800	1700	1900	1900	1600	1650	1900
Yield strength, psi	1300	1400	1450	1400	1400	1450	1400	1400	1400	1400
Elongation, %	500	450	500	500	500	500	500	450	450	500
Polyethylene, Pipe compound (3)										
Dielectric constant										
At 10^6 cps	2.8	2.8	--	2.7	3.0	3.0	2.7	2.9	--	2.7
At 5×10^7 cps	--	--	--	2.6	0.0	--	2.7	--	--	2.7
Dissipation factor										
At 10^6 cps	0.002	0.002	--	0.002	0.003	0.003	0.002	0.002	--	0.003
At 5×10^7 cps	--	--	--	0.007	--	--	0.110	--	--	0.012
Tensile strength, psi	2000	1900	2000	2000	1850	2000	1900	1850	1950	1900
Yield strength, psi	1350	1450	1500	1500	1400	1500	1400	1400	1500	1400
Elongation, %	600	600	575	600	550	600	550	550	525	550

(1) Determined by standard ASTM test methods. Typical values for dissipation factor at 5×10^7 cps are:
Polyethylene, natural - 0.0001
Polyethylene + 3 % carbon black - 0.0002 (optimum value).
When the dissipation factor at 5×10^7 cps exceeds 0.005, there are irregularities in distribution pattern of the carbon black.

(2) Electrical formulation: P124-3-1 (black) melt index 1.7; 3.0 % by weight Monarch 74 carbon black and 0.07 % N, N' diphenyl-P-phenylenediamine.

(3) Pipe compound: 651A-B131-X1 (black) . 2 % carbon black and 0.25% Age Rite White antioxidant. Melt index 1.7.

(*) Too high to measure.

(--) Not measured.

Outdoor weathering tests were conducted on six polyethylene formulations at two sites. Results are given in Table 32. (35) The data indicates little loss in the PC 51's properties after three years. The natural formulations degraded significantly, and the linear polyethylene Q 915.3 with 2 1/2 percent carbon black had extensive loss of elongation.

Table 33 contains the results of extensive testing (16 years) of various carbon black pigmented polyethylene formulations. All outdoor exposure was conducted at Murray Hill, New Jersey, at an angle of 45° facing south. Accelerated weathering was performed per ASTM E 42-57 in a modified XIA Weather-Ometer, an unshielded carbon-arc weathering machine.

TABLE 32. OUTDOOR WEATHERING OF BRANCHED AND LINEAR POLYETHYLENE (35)

Property	Branched Polyethylene							Linear Polyethylene						
	PC-51 Black Pipe Compound							Q-911.15						
		Arizona Exposure			Midland Exposure				Arizona Exposure			Midland Exposure		
	Blank	6 mo	1 yr	3 yrs	6 mo	1 yr	3 yrs	Blank	6 mo	1 yr	3 yrs	6 mo	1 yr	3 yrs
Yield tensile strength, psi	1,700	1,700	1,600	*	1,700	1,600	1,400	5,500	5,000	5,000	5,300	5,000	5,000	5,100
Tensile strength, psi	1,700	1,700	1,600	*	1,700	1,600	1,600	5,500	5,000	5,000	5,300	5,000	5,000	5,100
Elongation, %	165	160	160	*	160	160	150	30	15	14	11.5	15	12	17
	Polyethylene 700M							Q-913.4						
Yield tensile strength, psi	1,800	1,600	1,050	*	1,700	1,400	*	3,900	2,100	1,600	750	3,600	1,650	650
Tensile strength, psi	1,800	1,600	1,050	*	1,700	1,400	*	3,500	2,100	1,600	750	3,600	1,650	650
Elongation, %	125	140	20	*	125	110	*	30	2.0	1.0	0.5	6.0	1.5	1
	Polyethylene 900M							Q-915.3						
Yield tensile strength, psi	1,400	1,500	950	*	1,400	1,250	*	2,400	2,800	3,000	3,000	2,400	3,000	*
Tensile strength, psi	1,400	1,500	950	*	1,400	1,250	*	1,900	2,000	3,000	1,800	1,900	3,000	*
Elongation, %	110	120	25	*	110	140	*	3,000	50	50	65	250	75	*

*Test specimens were not available.

Note:
Q-911.15 - 2 1/2% carbon black
Q-913.4 - natural, melt index 1.2
Q-915.3 - 2 1/2% carbon black
700M - Natural, melt index 7.0
900M - Natural, melt index 20
PC51 carbon black + antioxidant

All materials were molded into ASTM test for specimens and sent to weathering stations in Arizona and Michigan. Samples were exposed at an angle of 45° south.

TABLE 33. TEST RESULTS ON WEATHERED 16 YEARS BLACK POLYETHYLENE SAMPLES (36)

Carbon Black Type	WT % C.B.	Background Dispersion[3]	Low Temperature Brittleness T_B[1]													
			Original			Weatherometer			Outdoor Exposure			Outdoor Exposure				Antioxidants[4]
			Tensile Strength[2]	% Elong	T_B	100 hr	200 hr	400 hr	1.5 yrs	8 yrs	16 yrs	8 years		16 years		
												T.S.	% Elong	T.S.	% Elong	
Paris	1	A	1955	650	-74	-65	-49	-45	-65	-69	>70	1525	635	1660	30	
Kosmos BB	0.1	B	1910	635	-74	-38	-16	0	-20	>70	5	1290	90	-	-	
"	2.0	B	1780	605	-74	-70	-59	-60	-60	-65	75	1700	660	1585	580	
"	5.0	B	1910	620	-74	-70	-65	-55	-60	-65	-55	1900	665	1675	560	
Micronex MPC	0.1	B+	1935	665	-74	-33	-16	>70	-15	>RT	RT	1250	55	-	-	
"	0.2	B	1930	660	-74	-40	-10	>70	-15	0	RT	1360	80	-	-	
"	0.3	B	1890	650	-74	-60	-45	-40	-65	49	-30	1500	185	1605	110	
"	1.0	B	1950	640	-74	-69	-35	-60	-65	-70	-65	1680	630	1610	570	
"	2.0	C	1905	630	-74	-49	-45	-40	-60	-65	-55	1700	650	1620	580	
"	5.0	B	1875	630	-72	-46	-44	-40	-60	-67	-65	1800	630	1670	540	
Philblack A	0.1	F	1970	630	-74	-20	+6	-	0	RT	RT	435	45	-	-	
"	0.2	F	1870	635	-74	-20	-10	>0	-5	>RT	RT	1250	75	-	-	
"	0.5	F	1835	665	-71	-43	-30	-25	-25	0	0	1515	-90	1468	0	
"	1.0	F	1870	640	-73	-60	-31	-25	-60	-45	-35	1585	225	1497	210	
"	2.0	F	1850	645	-74	-39	-35	-35	-60	-55	-65	1525	475	1555	530	
"	5.0	F	1745	575	-73	-56	-50	-45	-65	-70	-65	1660	530	1640	550	
Thermax	0.1	F	1885	660	-74	+4	-	-	-5	RT	-	-	-	-	-	
"	0.2	F	1970	670	-74	+4	-	-	-5	RT	-	-	-	-	-	
"	0.5	F	1860	660	-74	>0	-	-	0	RT	-	1030	70	-	-	
"	1.0	F	1565	520	-74	-39	-9	-10	-5	0	RT	1480	80	-	-	
"	2.0	F	1815	595	-74	-32	-24	-20	-40	0	0	1485	335	1450	0	
"	5.0	F	1885	635	-74	-55	-30	-25	-60	-30	-25	1595	220	1170	50	
"	1.0	F	1860	635	-74	-60	-50	-50	-30	-20	-25	1360	95	1350	60	Akroflex C
"	1.0	F	1870	670	-74	-69	-55	-50	-10	+10	>0	1325	65	-	-	Neozone D
"	1.0	F	1940	670	-74	-69	-59	-55	-60	0	RT	1375	70	1335	70	JZF
Philblack A	1.0	F	1875	610	-74	-69	-56	-50	-70	-55	-55	1590	550	1560	230	Akroflex C
"	1.0	F	1810	620	-74	-60	-51	-40	-55	-25	-15	1490	175	1550	100	Neozone D
"	1.0	F	1895	660	-74	-60	-50	-45	-76	-35	-25	1475	150	1530	110	JZF
Micronex MPC	1.0	B	1845	610	-74	-61	-54	-55	-70	-68	-65	1580	620	1590	540	Akroflex C
"	1.0	B	1815	615	-73	-70	-56	-50	-65	-55	-45	-	-	1525	460	Neozone D
"	1.0	B	1850	670	-74	-76	-60	-55	-55	-50	-55	1480	295	1520	160	JZF

[1] Low temperature brittleness - Tested in accordance with ASTM D746.

[2] Tensile strength and ultimate elongation - Tested in accordance with ASTM D412.

[3] Carbon black dispersion - Tested in accordance with MS17,000 Section 1059 using the following scale for rating of background dispersion:

Dispersion Rating	Sample Appearance at 100X
A	Very uniform, smooth and continuous color, no large particles
B	Smooth and continuous color, scattered large particles
C	Color discontinuous and varying in tone, large particles
F	"Salt and pepper" appearance, no continuous color

[4] Antioxidants	Structure
JZF	N-, N'-diphenyl-p-phenylenediamine
Neozone D	N-phenyl-beta-nahphtylaimine
Akroflex C	35% JZF 65% N-Phenyl-alpha-naphthylamine

Trade Name	Type	Av. Particle Diameter (mu)
Kosmos BB	Medium Color Channel	16-18
Micronex MPC	Medium Processing Channel	25-28
Philblack A	Fast Extrusion Furnace	51-58
Thermax	Medium Thermal	320-470

The test results indicate the following: (36)

- The low temperature properties of samples containing 0.1 percent channel black were very poor after 1.5 years outdoor exposure. Those containing less than one percent medium channel black were seriously degraded in less than eight years.

- Formulations containing medium channel black concentrations above one percent resulted in very good low temperature and tensile properties after 16 years outdoor exposure.

- The properties of samples containing furnace black improve with increasing pigment concentration, and require at least two percent concentration for 16 years protection.

- The medium thermal black formulations weathered poorly even with concentrations of five percent.

- The data agree with similar samples weathered in accelerated tests. That is, the finer the carbon black particle size for a given concentration of carbon black, the better the weather resistance. Also, the dispersion rating system is meaningful in predicting the relative effectiveness of carbon blacks as ultraviolet screeners.

- The addition of amine-type antioxidants (JZF and Neozone D) to medium channel black formulations did not improve their weatherability, but actually accelerated degradation. The results with the Akroflex C sample were not as conclusive and its effect could not be determined without further testing.

- The antioxidants reacted similarly with the furnace black except for those containing Akroflex C, which showed definite improvement.

- Antioxidants with Thermax indicated no improvement with Neozone D, slight with JZF, and the best with Akroflex C.

- Antioxidants can improve the weatherability of polyethylene but improvement depends on the choice of carbon blacks and the antioxidants used.

A comparison of the accelerated indoor weathering with outdoor exposure is depicted in Figure 48.

Table 34 shows the results of various pigments incorporated at 1 percent and 0.1 percent concentration in 0.96 density polyethylene (0.6 - 0.8 melt index). Tints were prepared with 1 percent titanium dioxide to the above formulation. This data was compared with 1 percent of each pigment in low density DYNH polyethylene (2.4-1.5 melt index, 0.919 density). Samples were compression molded into 40 and 75 mil plaques and exposed in Florida and a XIA Weather-Ometer. (37)

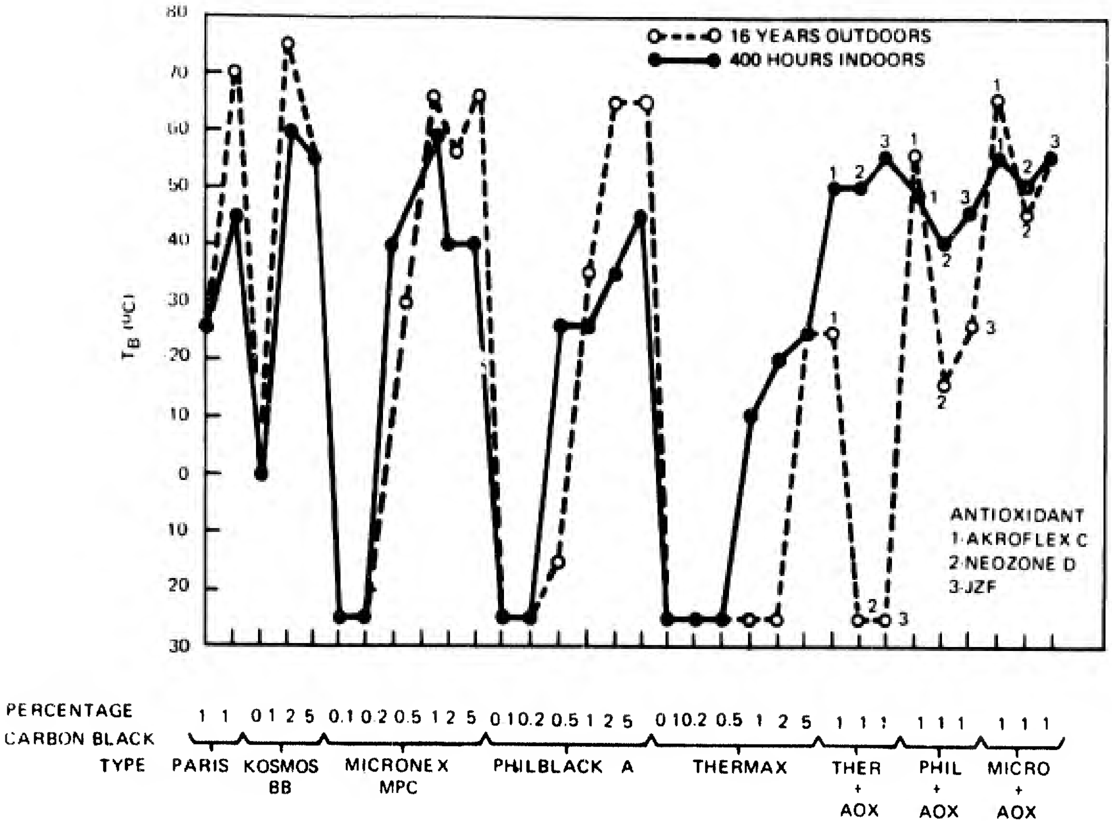


Figure 48. Overall comparison between indoor accelerated and outdoor weathering (36)

From Table 34 the following was observed: (37)

- Embrittlement - Phthalocyanine green and blue, a synthetic iron oxide and carbon black were superior in .96 density polyethylene. Cadmium sulfide selenide red, and strontium chromate yellow were satisfactory. Titanium dioxide alone was poor but tints made with it performed better than the pure color.

- Crazing - All colorants performed well in high density polyethylene but only cadmium sulfide, titanium dioxide and carbon black were suitable for DYNH.

- Color - All colorants except strontium chromate were satisfactory in high density polyethylene. Metallic oxide (pink) and the yellow pigments failed in DYNH.

Tensile specimens containing up to 2 percent of various pigments were exposed on a laboratory roof in Pennsylvania for three years. The results in Table 35 were compared with specimens aged 1500 hours in the dark at 73°F and 1500 hours in a Fade-Ometer. (38)

The samples containing carbon black, as would be expected, resisted outdoor and Fade-Ometer exposure better than any other pigment. The next best protection was obtained with phthalo blue (1.0 and 2.0 percent) and 2.0 percent concentrations of cadmium red, cadmium orange and red iron oxide. The tensile elongations of all other samples were extremely reduced by both types of weathering.

TABLE 34. EFFECT OF OUTDOOR AND ACCELERATED EXPOSURE ON VARIOUS PIGMENTED POLYETHYLENES (37)

RM Code No.	LEGEND		EMBRITTLEMENT					CRAZING				
	COLORANT	COLORANT TYPE	1%	0.96 Density Polyethylene Tint	0.1%	Tint	DYNH	1%	0.96 Density Polyethylene Tint	0.1%	Tint	DYNH
78AB	Strontium Chromate M-1651	Strontium Chromate	1250	1250	750	750	750+	1250+	1250+	750+	750+	750
78AG	Cadmium Golden Yellow	Cadmium Sulfide	6000+	3500+	3500+	1250	1250+	3000	2000	2000	1250+	1000
78AC	Green Gold YT-562-D	Nickel Azo Complex	2500+	1500+	1250+	750+	4000+	1750	1500	1250+	750+	1000
84G	Opaline Green G-1	Phthalocyanine	3500+	3000+	1500+	2250+	2500+	2000	1750	1500+	1750	750
84J	Chromic Oxide Green X-1134	Chromium Oxide	2250+	2750+	1500+	1250+	4000	1250	1750	1300+	1250+	750
70X	Bonnie Blue D-2211	Cobalt	2000+	4000+	2000+	1750+	3500	80	2000	80	1750	750
70AB	Monastral Blue BT-380-D	Phthalocyanine	5000+	4000+	3500+	3000+	1500+	1750	2000	1750	1750	750
34AL	Bright Red 10150	Cadmium Sulfide Selenide	3500+	2250+	1500+	2500+	--	1750	1750	1500	1500	--
34I	Indian Red R-8098	Synthetic Iron Oxide	1500+	1750+	1500+	4000+	1000+	1500	1500	1500+	1750	500
34AJ	Pink F-4889	Metallic Oxide Combination	2000+	4000+	2000+	1750+	500+	1750	2000	1250	1750	500+
34U	Cadmium Selenide Red 1120	Cadmium Sulfide Selenide	6500+	4000+	2000+	4000+	4500+	2250	2500	2000	2250	1250
34AM	Deep Red 10156	Cadmium Sulfide Selenide	4000+	2750+	2000+	2500+	2250+	2000	2250	1750	2250	1500
34R	Light Red Oxide R-2899	Synthetic Iron Oxide	4500+	3500+	2250+	3250+	5500+	2250	2000	2250	2250	1000
41Z	Ti Pure R-110	Rutile Titanium Dioxide	5000+	--	5000	--	3250+	1750	--	1750	--	750
41R	Unitane 0-310	Anatase Titanium Dioxide	5000+	-	5000+	-	4000	1500+	--	2000	--	750
32AB	Micronex Beads W-6	Easy Processing Channel Black	10000+	6000+	3000+	2250+	5000+	1250	1250	750	750	2000
32G	Monarch 74	Medium Color Channel Black	10000+	6000+	4000+	2250+	5000+	1250	1250	1250	1250	5000
79K	Albron 408	Aluminum	2500+	2500+	2500+	2250+	3000+	1500	1750	1250	1500	1000
CONTROL				2500			4000+		1500			1500

FLORIDA WEATHERING DATA

	EMBRITTLEMENT					CRAZING					COLOR CHANGE					
RM Code No.	1%	0.96 Density Polyethylene Tint	0.1%	Tint	DYNH 1%	1%	0.96 Density Polyethylene Tint	0.1%	Tint	DYNH 1%	1%	0.96 Density Polyethylene Tint	0.1%	Tint	DYNH 1%	Type of Color Change
78AB	1500	1500	750	750	500+	1500	1500+	750+	750+	500+	1000	1000	500	320	320	Darkening
78AG	750	750	750	750	1500+	2250	1750+	1500+	1550+	1500	3000+	1500	1000	1000	1000	Fading
78AC	500	750	750	750	3700+	2250	1500+	1500+	1500+	1000	2750	1000	750	750	3700+	Fading
84G	3000+	3000+	750	750	3000+	3000+	3000+	3000+	3000+	750	3000+	3000+	3000	3000	3000+	Fading
84J	750	1000	750	750	3000+	2250	2250	2500	2500	750	3000+	3000+	3000	3000+	3000+	Fading
70X	500	2000	500	1000	2000+	2000+	3000+	2250+	2500	1000	1750	3000+	2000	3000+	1750	Fading
70AB	2000	2000	1750	1750	3000+	3000+	3000+	3000+	3000+	750	3000+	3000+	3000+	3000+	3000+	Fading
34AL	1500	2000	750	1500	3000+	2800	3000+	1750+	2800	1000	3000+	3000+	1500	3000+	2250	Fading
34I	750	750	750	750	2000+	2500	2500	2500	2250	1000	3000+	3000+	2250	3000+	1750	Fading
34AJ	500	1000	1000	1000	3000	2250+	2500	1750+	2500	1000	2000	3000+	1500	3000+	320	Fading
34U	1000	2000	1000	1000	2250+	2500	2250+	1750+	1750+	1000	3000+	2000	1500	1500	2000	Fading
34AM	1000	2250	1000	1000	2250+	2500	2500	2250+	2500	1000	3000+	3000+	2000	3000+	2000	Fading
34R	3000+	3000+	750	1500	3000+	3000+	3000+	2250	2250	750	3000+	3000+	2250	3000+	2000	Fading
41Z	750	--	750	--	1000	2500	--	3000+	--	1500	3000+	--	3000+	--	3000	Darkening
41R	500	--	750	--	1000	3000+	--	3000+	--	1500	3000+	--	3000+	--	2000	Darkening
32AB	3000+	3000+	2250	3000+	3000+	3000+	3000+	3000+	3000+	2000	3000+	3000+	3000+	3000+	3000+	Fading
32G	3000+	3000+	3000+	3000+	3000+	3000+	3000+	3000+	3000+	3000+	3000+	3000+	3000+	3000+	3000+	Fading
79K	500	1000	500	1000	3000+	2250	2250	2250	2250	750	3000+	3000+	3000+	3000+	3000+	Fading
Control		750			3000+		2500			1500			3000+		2250	Darkening

Note: Values indicated above represent the number of exposure hours to yield moderate embrittlement, crazing and color change. At this point, specimens are still considered acceptable, although further change would constitute failure.

Plus signs indicate samples have not yet evidenced moderate embrittlement, crazing and color changes.

TABLE 35. EFFECT OF VARIOUS PIGMENTS ON ULTRAVIOLET DEGRADATION OF POLYETHYLENE (SUPER DYLAN)* (38)

Super Dylan Polyethylene, RPD-55 60T 9-E-26 Sample Number	Pigment Additive Type	%	Unexposed Specimens		Specimens Aged in Dark for 1, 500 Hours @ 73°F		Specimens Exposed on Product Development Laboratory Roof (Penna.) for Three Years				Specimens Exposed in a Fade-Ometer for 1, 500 Hours			
			Tensile Strength at Yield, PSI	Ultimate Elongation, %	Tensile Strength at Yield, PSI	Ultimate Elongation, %	Tensile Strength at Yield, PSI	Estimated 95% Population Limits	Ultimate Elongation, %	Estimated 95% Population Limits	Tensile Strength at Yield, PSI	Estimated 95% Population Limits	Ultimate Elongation, %	Estimated 95% Population Limits
1A	Black	0.5	3, 570	187	3, 300	284	3, 540	±190	260	±184	3, 500	±180	189	±67
1B		1.0	3, 510	271	3, 320	266	3, 580	±20	241	±112	3, 520	±90	147	±88
1C		2.0	3, 610	239	3, 420	141	3, 600	±80	318	±102	3, 510	±170	224	±168
2A	White Rutile	0.5	3, 080	322	3, 280	212	2, 150	±480	6	±8	2, 040	±570	3	±3
2B		1.0	3, 080	385	3, 270	344	2, 490	±560	6	±7	2, 620	±550	6	±2
2C		2.0	3, 510	237	3, 450	357	3, 430	±250	9	±4	3, 460	±230	16	±2
3A	White Anatase	0.5	3, 340	201	3, 290	224	1, 570	[illegible]	1	±1	2, 450	±1, 040	4	±5
3B		1.0	3, 280	205	3, 400	206	1, 820	±230	2	±3	2, 670	±860	6	±7
3C		2.0	3, 430	318	3, 390	234	2, 290	±260	3	±3	2, 320	±760	4	±3
4A	Phthalo Blue	0.5	3, 400	338	3, 520	459	3, 520	±90	295	±114	3, 660	±30	92	±60
4B		1.0	3, 490	595	3, 500	591	3, 530	±70	399	±360	3, 660	±40	267	±43
4C		2.0	3, 550	358	3, 530	417	3, 540	±100	214	±175	3, 650	±10	216	±95
5A	Phthalo Green	0.5	3, 320	289	3, 370	316	1, 680	±250	5	±4	2, 390	±220	4	±2
5B		1.0	3, 360	617	3, 400	527	2, 320	±60	9	±2	2, 650	±330	5	±2
5C		2.0	3, 380	434	3, 180	409	2, 680	±60	11	±2	2, 200	±370	2	±2
6A	Ultramarine Blue	0.5	3, 380	439	3, 320	312	1, 140	±20	1	±1	2, 430	±160	2	±2
6B		1.0	3, 380	300	3, 300	307	1, 190	±50	2	±2	2, 080	±200	2	±1
6C		2.0	3, 370	340	3, 280	410	1, 300	±110	3	±1	2, 330	±310	3	±3
7A	Chromium Oxide Green	0.5	3, 330	302	3, 200	470	2, 540	±180	12	±1	2, 350	±210	3	±2
7B		1.0	3, 380	401	3, 230	508	3, 000	±110	26	±9	3, 450	±80	21	±20
7C		2.0	3, 390	244	3, 190	411	3, 380	±20	64	±8	3, 800	±30	96	±25
8A	Cadmium Yellow	0.5	3, 430	289	3, 370	186	1, 920	±110	2	±2	3, 420	±200	7	±3
8B		1.0	3. 340	244	3, 360	223	3, 350	±130	22	±7	3, 850	±110	58	±12
8C		2.0	3, 530	204	3, 380	239	3, 510	±130	51	±4	3, 620	±40	92	±43
9A	Cadmium Red	0.5	3, 410	319	3, 450	378	2, 620	±450	5	±5	2, 920	±200	6	±3
9B		1.0	3, 340	278	3, 280	230	3, 550	±30	44	±9	3, 450	±40	47	±6
9C		2.0	3, 390	244	3, 420	227	3, 480	±90	371	±134	3, 450	±160	121	±21
10A	Cadmium Orange	0.5	3, 410	261	3, 330	194	2, 870	±270	5	±5	3, 480	±200	33	±12
10B		1.0	3, 330	267	3, 422	406	3, 500	±110	116	±77	3, 420	±110	76	±39
10C		2.0	3, 360	318	3, 410	372	3, 480	±170	292	±156	3, 470	±40	135	±73
11A	Red Iron Oxide	0.5	3, 410	263	3, 410	274	3, 160	±100	14	±5	2, 650	±180	5	±2
11B		1.0	3, 360	185	3, 280	411	3, 370	±140	81	±53	3, 420	±40	62	±3
11C		2.0	3, 340	424	3, 190	440	3, 390	±120	377	±217	3, 420	±100	157	±145
12	Blank	-	3. 430	315	3, 240	338	Specimens Deteriorated From Exposure - Not Suitable for Evaluating				1, 980	±510	4	±4
13	Blank	-	3, 440	232	3, 280	296	1, 030	±80	1	NIL	2, 220	±560	3	±2
14A	White Rutile (Made on Development Bolling Mill)	0.5	3, 350	160	3, 000	147	2, 230	±140	9	±2	2, 000	±470	3	±3
14B		1.0	3. 340	138	3, 340	143	2, 640	±380	7	±6	2, 600	±330	7	±4
14C		2.0	3, 360	152	3, 370	231	3, 200	±70	10	±1	3, 040	±100	13	±6

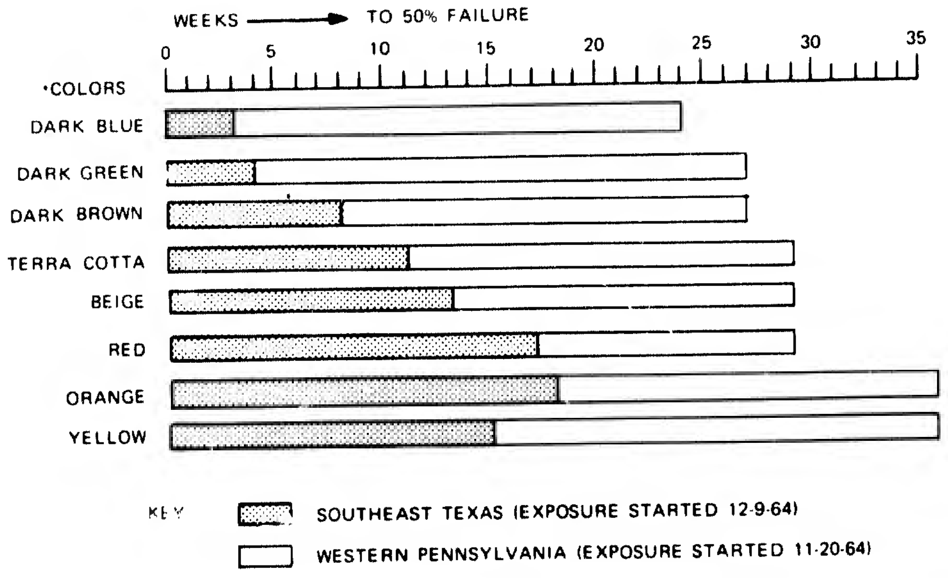
All samples except No. 12 contained an antioxidant. Samples No. 12 and 13 contained no pigment.

Figure 49 compares the screening ability of eight pigments systems with the same stabilizers at Southeast Texas and Western Pennsylvania exposures. (6) The weathering procedure was described on page 43. In examining this data it must be noted that the pigment concentrations were not kept constant.

The dark blue was the poorest in both locations, failing eight times faster in Texas than Pennsylvania. In contrast the orange pigment was the best in both locations, failing only twice as fast in Texas than Pennsylvania.

It was reported that standard 1/8" thick injection molded tensile bars molded from the same eight batches of colored polyethylenes were exposed simultaneously at the two outdoor locations and in a Fade-Ometer. After 52 weeks outdoor exposure and 2,000 hours in the Fade-Ometer, none of the eight colors exhibited significant deterioration in tensile properties. (6)

OUTDOOR WEATHERING BENT STRIP SPECIMENS



• BASE RESIN SUPER DYLAN® POLYETHYLENE 6530, 0.953 DENSITY, 3.0 MELT INDEX, HIGH DENSITY COPOLYMER, CONTAINING AN ULTRAVIOLET LIGHT ABSORBER PLUS PIGMENTS.

Figure 49. Screening ability of various pigment systems. (6)

Table 36 gives the life expectancy of various pigmented compositions at 1 percent concentration.

Figure 50 shows the percent of ultraviolet and visible light transmitted through two different thicknesses of stabilized and unstabilized polyethylene film.

TABLE 36. LIFE EXPECTANCY OF 0.96 DENSITY POLYETHYLENE, 0.06-0.07" THICK CONTAINING 1% PIGMENT (14)

Pigment	Life, months	
	Florida	Arizona
Phthalocyanine green	24	18
Cadmium Yellow	12	18
Cadmium Red	12	18
Titanium dioxide, anatase	4	3
rutile	6	6

End-point: Manual bend or 10% of tensile elongation retained, or 2/3 of tensile strength retained.

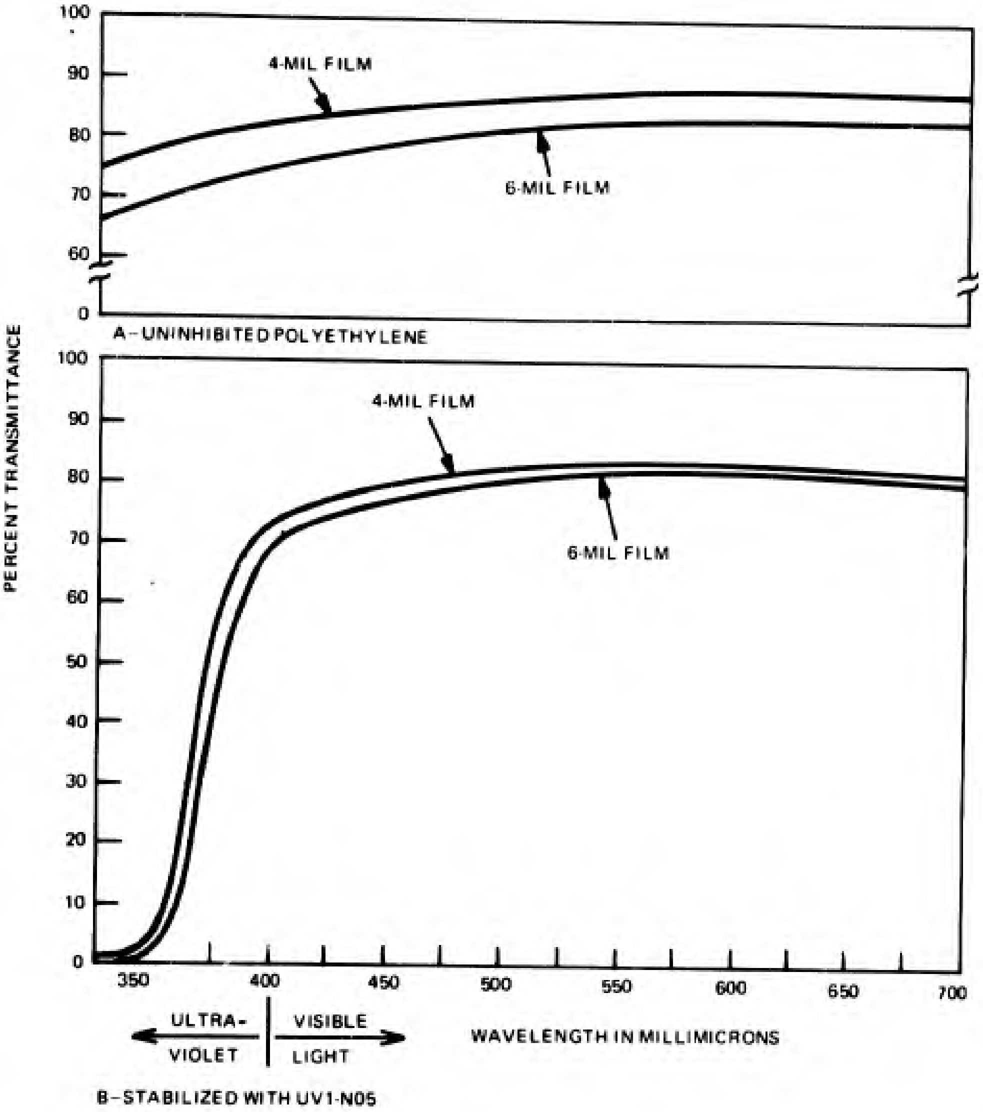


Figure 50. Transmission of visible and some ultraviolet light through uninhibited and stabilized (UV 1 NO 5) polyethylene plastic film (Tenite) (31)

High density polyethylene and high impact polypropylene were exposed three years at the U.S. Navy Research Testing Station, Panama, Canal Zone; White Sands, New Mexico; Fort Wainwright, Alaska; and Picatinny Arsenal, New Jersey. (39) All specimens were mounted on racks facing south and were inclined 45° from the horizontal.

Eight specimens from each exposure site were withdrawn every 12 months, conditioned 48 hours at 73.5 ± 2°F, 50 ± 4 percent relative humidity and tested in accordance with ASTM D638-61T. These data are compared in Table 37 to the initial values and results of eight samples stored three years in a dark air-conditioned room under standard conditions.

TABLE 37. EFFECTS OF THREE YEARS' OUTDOOR WEATHERING ON TENSILE PROPERTIES OF POLYOLEFINS (39)

Code No.	Material (Generic)	Site[b]	Data on tensile strength[a], psi					Data on percent elongation (to yield or break)[a]		
			Initial Controls	Final Controls (stored 3 years)	Weathered 1 year	Weathered 2 years	Weathered 3 years	Initial Controls	Final Controls (stored 3 years)	Weathered Sample (3 years outdoor exposure)
306	Polyethylene	PA	3135	3280 (+4.6%)	3100 (-0.9%)	3345 (+6.7%)	3345 (+6.7%)	9.50	8.50 (-10.5)	11.0 (+15.8)
610	Polypropylene	PA	4350	4530 (+4.2%)	4310 (-1.0%)	4660 (+7.0%)	4560 (+4.7%)	3.90	3.90 (0.0)	3.70 (-5.1)
613	Polypropylene	PA	3475	3550 (+2.1%)	3185 (-8.3%)	3180 (-8.5%)	3170 (-8.7%)	6.25	6.50 (+3.9)	5.75 (-7.8)
		Z	3475	3550 (+2.1%)	3230 (-7.1%)	3160 (-9.0%)	3250 (-6.4%)	6.25	6.50 (+3.9)	6.25 (0.0)
		W	3475	3550 (+2.1%)	3300 (-4.8%)	3225 (-7.2%)	3180 (-8.5%)	6.25	6.50 (+3.9)	6.00 (-3.8)
		A	3475	3550 (+2.1%)	3510 (+0.7%)	3370 (-3.0%)	3340 (-3.9%)	6.25	6.50 (+3.9)	5.25 (-15.9)
618	Polyethylene	PA	2985	3000 (+0.4%)	2985 (0%)	3010 (+0.7%)	3045 (+2.0%)	10.00	10.00 (0.0)	10.50 (+5.0)
		Z	2985	3000 (+0.4%)	3010 (+0.7%)	3065 (+2.8%)	3125 (+4.6%)	10.00	10.00 (0.0)	10.25 (+2.5)
		W	2985	3000 (+0.4%)	3030 (+1.5%)	3090 (+3.5%)	3145 (+5.3%)	10.00	10.00 (0.0)	11.50 (+15.0)
		A	2985	3000 (+0.4%)	2965 (-0.7%)	3010 (+0.7%)	3080 (+3.2%)	10.00	10.00 (0.0)	10.00 (0.0)
620	Polyethylene	PA	3020	3210 (+6.2%)	3070 (+1.6%)	3140 (+4.0%)	3160 (+4.6%)	11.50	11.50 (0.0)	11.50 (0.0)
		Z	3020	3210 (+6.2%)	3090 (+2.3%)	3150 (+4.3%)	3160 (+4.6%)	11.50	11.50 (0.0)	10.50 (-8.7)
		W	3020	3210 (+6.2%)	3110 (+3.0%)	3210 (+6.2%)	3210 (+6.2%)	11.50	11.50 (0.0)	11.00 (-4.3)
		A	3020	3210 (+6.2%)	3110 (+3.0%)	3090 (+2.3%)	3150 (+4.3%)	11.50	11.50 (0.0)	11.00 (-4.3)
621	Polyethylene	PA	3425	3460 (+1.0%)	3350 (-2.2%)	3375 (-1.5%)	3365 (-1.8%)	8.50	8.25 (-2.9)	7.75 (-8.8%)
		Z	3425	3460 (+1.0%)	3390 (-1.0%)	3230 (-5.5%)	3190 (-6.8%)	8.50	8.25 (-2.9)	8.25 (-2.9)
		W	3425	3460 (+1.0%)	3380 (-1.2%)	3280 (-4.2%)	3320 (-3.0%)	8.50	8.25 (-2.9)	8.25 (-2.9)
		A	3425	3460 (+1.0%)	3390 (+1.0%)	3470 (+1.2%)	3505 (+2.3%)	8.50	8.25 (-2.9)	8.75 (+2.9)

Note: Code No.	Material
306	Polyethylene, high-density homopolymer, stress crack resistant, dark green color
610	Polypropylene (high impact, high softening temperature), black color
613	Polypropylene (high impact, high softening temperature), marine green color
618	Polyethylene, high density, marine green color
620	Polyethylene, high density, marine green color
621	Polyethylene, high density, black color

[a] Figures in parentheses give percent tensile loss (-) or gain (+) compared to the tensile strength and elongation (to yield or break) of the initial controls.

[b] PA - Picatinny Arsenal; Z - Canal Zone; W - White Sands; A - Alaska.

[c] All specimens consisted of tensile bar conforming to type 1, method 1011, Fed. test Mtd. 406. Tests conducted in accordance w/ASTMD638-61T at crosshead speed of 0.2"/min.

Inasmuch as the polyolefin material was not identified by specification or supplier, the data lose some of their usefulness. However, it can be said that the polypropylenes (as would be expected) were inferior to the polyethylenes after weathering. The superiority of the Code No. 618 polyethylene sample shows that good weatherability can be obtained in a colored formulation. In this case it was much superior to the normal good black formulation.

Table 38 presents the tensile strength and yield elongation of four classes of unidentified commercial polypropylenes exposed 800 hours in a Weather-Ometer. Again, the usefulness of the data is limited but it does demonstrate the superiority of light resistant formulation.

TABLE 38. EFFECT OF ACCELERATED WEATHERING (ATLAS TWIN-ARC WEATHER-OMETER) ON THE TENSILE PROPERTIES OF POLYPROPYLENES (40)

Injection-molded Type I specimens; crosshead speed, 2 inches/mirute.				
	Tensile Properties After Indicated Nominal Weathering Time			
Sample	0 Hours	300 Hours	600 Hours	800 Hours
	Yield Tensile Strength, psi			
General Purpose				
A	4810 ± 60	5160 ± 30	4890 ± 30	2930 ± 40
B	4830 ± 90	4890 ± 30	4410 ± 50	3610 ± 100
C	4660 ± 50	4900 ± 120	4050 ± 510	3650 ± 90
D	4900 ± 60	3180 ± 770	3480 ± 250	2200 ± 200
E	4540 ± 20	4370 ± 290	3720 ± 500	3170 ± 110
Heat Resistant				
F	4610 ± 50	5030 ± 30	4700 ± 70	3770 ± 110
G	4800 ± 10	5090 ± 30	4760 ± 70	4090 ± 260
H	4840 ± 40	4900 ± 380	3200 ± 450	2690 ± 270
I	4330 ± 30	4480 ± 90	4070 ± 80	3570 ± 90
Light Resistant				
J	4530 ± 30	3870 ± 820	4420 ± 50	4280 ± 50
K	4630 ± 10	5040 ± 50	5150 ± 25	5070 ± 90
L	4520 ± 20	2670 ± 140	2190 ± 60	2200 ± 40
Impact Resistant				
M	3990 ± 30	2710 ± 140	3300 ± 80	3120 ± 30
N	3440 ± 60	2790 ± 180	2730 ± 70	2660 ± 10
O	3710 ± 40	3530 ± 40	3280 ± 80	3080 ± 20
	Yield Elongation, per cent			
General Purpose				
A	19.8 ± 0.5	13.5 ± 1.9	11.0 ± 0.5	14.9 ± 2.2
B	21.8 ± 1.0	13.2 ± 1.4	10.3 ± 0.3	7.3 ± 0.5
C	21.7 ± 1.0	13.7 ± 1.5	11.3 ± 0.7	7.0 ± 1.4
D	19.2 ± 1.1	2.0 ± 0.6	3.8 ± 0.8	1.2 ± 0.5
E	23.4 ± 0.3	10.8 ± 3.1	9.1 ± 1.9	7.3 ± 3.0
Heat Resistant				
F	18.8 ± 2.1	14.0 ± 0.0	11.2 ± 0.5	8.8 ± 1.0
G	20.9 ± 0.4	12.8 ± 0.7	9.2 ± 0.4	6.8 ± 0.8
H	20.3 ± 1.0	9.0 ± 4.1	2.7 ± 0.5	2.3 ± 0.8
I	23.9 ± 0.1	14.3 ± 0.8	10.6 ± 2.2	7.2 ± 1.4
Light Resistant				
J	18.7 ± 0.9	8.2 ± 5.9	11.3 ± 0.9	11.3 ± 0.9
K	18.1 ± 0.9	14.3 ± 0.5	14.5 ± 0.5	14.0 ± 1.4
L	19.8 ± 0.5	7.0 ± 0.6	6.0 ± 1.1	7.8 ± 6.9
Impact Resistant				
M	20.5 ± 0.3	2.2 ± 0.4	9.1 ± 1.1	7.7 ± 0.5
N	17.9 ± 0.3	5.3 ± 2.7	6.8 ± 1.2	7.3 ± 0.8
O	30.3 ± 0.5	21.1 ± 1.4	17.8 ± 1.4	15.8 ± 1.8

Table 39 compares weather resistance of ethylene/ethyl acrylate copolymer and low density homopolymer polyethylene. It is interesting to note that the natural copolymer is better in retaining its elongation properties whereas the homopolymer retains its tensile strength better. The carbon black and ultraviolet stabilized bars had good retention of properties after six months of Arizona exposure. The addition of 1.0 percent Ti O_2 did not improve weatherability.

TABLE 39. WEATHER RESISTANCE OF ZETAFIN 30, ZETAFIN 70 AND DOW POLYETHYLENE 900M INJECTION MOLDED TEST BARS (41)

Material	Exposure 45° South, Arizona years	Exposure 45° South, Arizona Langleys	Tensile Strength psi	Elongation, %	Remarks, Appearance
Zetafin 30, Natural (.928 density 2.5 melt index)	0	0	1,475	152	6 month - All samples bowed otherwise the same as unexposed samples. 1 year - All samples quite badly cracked. 2 years - All samples badly cracked. (Cracking occurred on all surfaces, front, side & back).
	1/2	92,236	800	149	
	1	193,739	450	43	
	2	385,053	335	29	
Zetafin 70, Natural (.929 density, 18.5 melt index)	0	0	1,350	136	same
	1/2	92,236	1,250	97	
	1	193,739	370	47	
	2	385,053	290	24	
Dow Polyethylene 900M (.915 density, 20.0 melt index)	0	0	1,125	105	same
	1/2	92,236	780	68	
	1	193,739	850	23	
	2	385,053	600	10	
Zetafin 30 Natural + 1.0% Carbon black (9PE - 1363)	0	0	1,325	150	Black Surface appearance unchanged.
	1/2	99,100	1,375	165	
Zetafin 30 Natural + 2.5% carbon black (9PE - 1363)	0	0	1,325	160	Black Surface appearance unchanged.
	1/2	99,100	1,375	150	
Zetafin 30 Natural + 1.0% T_iO_2 (conc.)	0	0	1,350	155	White Moderate yellow and many fine cracks.
	1/2	99,100	830	80	
Zetafin 30 Natural + 3/4% Ultraviolet absorber	0	0	1,250	155	Intermediate haze - Faint yellow. Slight yellow color.
	1/2	99,100	1,300	155	

Note: Zetafin - ethylene/ethyl acrylate copolymer tensile properties were obtained at a crosshead speed of 10.0 inches 1 minute on the Instron testing machine using a gage length of 2.0 inches and a span of 4.5 inches. Elongation measured with dividers. Test method: ASTM D638 - 61T.

The Ministry of Aviation has compared the results of two, one year tropical exposure tests of press-polished polyethylene (polythene) sheet material. (7) The first tests were conducted in 1957-58 in Nigeria, West Africa and the second in 1963-64 in Queensland, Australia.

A description of the material is given in Table 40.

TABLE 40. DESCRIPTION OF POLYTHENES (7)

Materials	Melt Flow Index	Density	Carbon Black %	Remarks
Alkathene 2	2.18	0.9173	-	Clear (pink)
Alkathene 2	2.18	0.9173	2 1/2	Good dispersion
Alkathene 0.2	0.27	0.9206	-	Clear (red)

Note 1 The Carbon Black used in Batch B was 'Kosmink' (a conductive channel black).

Note 2 All three batches contained anti-oxidant (0.2 per cent of 'Nonox C.I., i.e. NN'-di-β-naphthyl paraphenylene diamine).

Note 3 The melt flow index was determined according to Method 105C of B.S. 2782; the measurements of density were carried out in a density column at 23°C.

The samples were exposed in Nigeria at a 45° angle to the horizontal facing south; and at 45° to the horizontal facing north in Australia. A comparison of the weathering data at four sites is given in Table 41.

TABLE 41. WEATHER DATA AT HOT/WET & HOT/DRY SITES (7)

	Hot/Wet		Hot/Dry	
	Port Harcourt Nigeria	Innisfail Australia	Kano Nigeria	Cloncurry Australia
Mean annual temperature °F	79	74	80	78
Mean diurnal temperature range	13	18	26	26
Annual temperature range	5	15	16	27
Annual extreme temperature range	31	56	60	72
Mean diurnal R.H. range	16	36	41	31
Mean maximum R.H.	95	97	72	56
Mean minimum R.H.	79	61	31	25
Total rainfall (inches)	99	147	36	13
Total sun hours	396	2472	3200	3450

Samples were withdrawn every three months and measured for changes in weight, dimensions, tensile strength, elongation-at-break, permittivity and power factor as well as general appearance.

The data in Tables 42 and 43 indicate that the clear polyethylene samples degraded more at the Queensland hot/dry site at Cloncurry than at the Nigerian site, Kano; and much more severely at the Queensland hot/wet site, Innisfail than at Port Harcourt, Nigeria. The carbon black formulation weathered best and is suitable for tropical use. However, even the carbon black formulations performed slightly better at the Nigerian sites than at the Queensland sites.

TABLE 42. EFFECT OF HOT/WET SITES: PORT HARCOURT VS INNISFAIL (IN CLEARING) ON POLYETHYLENE PROPERTIES (7)

Grade of Polymer	Exposure, Months	Tensile Strength lb sq. in.		Elongation at Break, %[1]		Power Factor[2]		Permittivity[2]		% Change in Weight		% Change in Dimensions	
		P.H.	I	P.H.	I	P.H.	I	P.H.	I	P.H.	I	P.H.	I
Alkathene 2 Clear	0	1600	1810	520	545	.0001	.00015	2.31	2.37	-	-	-	-
	3	1600	1670	520	480	.0003	.00072	2.32	2.38	-0.11	-0.04	-0.2	-0.3
	6	1920	1330	530	85	.0003	.0015	2.35	2.38	-0.05	-0.07	+0.1	-0.4
	12	1720	1530	270	30	.0006	.0038	2.35	2.35	+0.07	-0.39	-0.2	-0.8
Alkathene 2 Black	0	1830	1975	530	585	.021	.0059	2.64	2.62	-	-	-	-
	3	1660	1770	560	560	.021	.0062	2.60	2.61	-0.11	-0.43	-0.3	-0.6
	6	1750	1485	500	535	.021	.0057	2.66	2.63	-0.10	-0.50	-0.4	-0.7
	12	1920	1860	540	535	.021	.0066	2.65	2.59	-0.06	-0.68	-0.4	-0.7
Alkathene 0.2 Clear	0	2080	2090	520	595	.0001	.00021	2.34	2.36	-	-	-	-
	3	2210	1375	540	145	.0003	.0011	2.33	2.35	-0.07	-0.26	-0.2	-0.5
	6	2260	1055	570	20	.0003	.0016	2.37	2.53	-0.09	-0.39	-0.1	-0.7
	12	2140	1355	490	25	.0005	.0047	2.36	2.38	-0.04	-0.85	-0.1	-0.9

[1] Specimens conformed to dumb-bell C B S 903, 1950 part 15 - Tested on Goodbrand pendulum-type machine at rate of strain of 10" per min at 20°C.

[2] Meas. at 10 metgacycles in seconds (BS2067).

After one year's exposure at the sites, the appearance of Alkathene 2 formulation with carbon black was unchanged. The material's appearance without carbon black at the hot/wet sites showed:

Innisfail -Initial rapid darkening in color followed by almost complete fading to off-white. Also, extensive cracking of the upper surface exposed to the sun. There was also a thin network of black biological growth.

Port Harcourt - The color changed to dark brown but did not subsequently fade. No surface cracking but heavy biological growth (particularly algal) was observed.

TABLE 43. EFFECT OF HOT/DRY SITES: KANO VS CLONCURRY ON POLYETHYLENE PROPERTIES (7)

Grade of Polymer	Exposure, Months	Tensile Strength lb/sq. in.		Elongation at Break, %[1]		Power Factor[2]		Permittivity[2]		% Change in Weight		% Change in Dimensions	
		K	C	K	C	K	C	K	C	K	C	K	C
Alkathene 2 Clear	0	1600	1810	520	545	.0001	.00015	2.31	2.37	-	-	-	-
	3	1400	1325	320	95	.0010	.0014	2.38	2.36	+0.01	-0.10	-0.1	-0.2
	6	1600	1170	70	45	.0020	.0025	2.40	2.54	-0.02	-0.17	-0.3	-0.3
	12	1110	1420	20	25	.0040	.0050	2.40	2.43	-0.26	-0.68	-	-0.7
Alkathene 2 Black	0	1630	1975	530	565	.021	.0059	2.64	2.62	-	-	-	-
	3	1820	1575	530	570	.021	.0068	2.68	2.61	-0.03	-0.50	-0.2	-1.3
	6	1630	1490	540	585	.020	.0070	2.63	2.61	-0.16	-0.61	-0.2	-1.4
	12	1840	1790	550	540	.022	.0069	2.65	2.57	-0.27	-0.79	-0.3	-1.7
Alkathene 0.2 Clear	0	2080	2090	520	595	.0001	.00021	2.34	2.36	-	-	-	-
	3	1870	1455	430	70	.0005	.0014	2.37	2.36	-0.03	-0.40	+0.1	-0.9
	6	1770	1090	80	20	.0013	.0025	2.36	2.49	-0.09	-0.55	-0.3	-0.8
	12	1190	1450	20	20	.0026	.0067	2.40	2.42	-0.23	-1.18	-0.3	-1.3

1. Specimens conformed to dumb-bell C.B.S. 903, 1950 part 15 - Tested on Goodbrand pendulum - type test machine at rate of strain of 10" per min. at 20°C.
2. Meas. at 10 metacycles in second (BS2067).

The appearance at the hot/dry sites were:

Cloncurry - Darkened to medium brown and then faded to off-white. Surface cracks and warping were severe on the upper surface.

Kano - Developed a milky appearance, then darkened with no fading taking place. Serious cracking and warping were also reported.

The above differences in weatherability can be related to the total number of sun hours reported at the different sites and the known ultraviolet radiation. That is, the specimens exposed at the Australian sites received a higher amount of utlraviolet radiation than those in West Africa. (7)

Table 44 reports on 4.5 years exposure at Murray Hill, New Jersey, of two unidentified commercial polyolefins. As can be seen, the polyethylene weathered well but the polypropylene losts its flexibility in a short time. This is due to chain scission. (42)

TABLE 44. EFFECT OF OUTDOOR AGING AT MURRAY HILL, N.J. 1/ ON STIFFNESS OF POLYOLEFINS 2/ (42)

	Initial Stiffness, psi ASTMD747	Percent Change		
		1.5 Yrs	3 Yrs	4.5 Yrs
Polyethylene, Black	117,300	-0.4	-0.8	+0.6
Polypropylene, Ivory	153,500	-12.0	-22.0	-26.9

1/ Exposed on stainless steel holders, exposed at 45^{o} angle facing south.

2/ Specimens were inj molded, cut & milled to 0.25" width; conditioned 2 weeks at $23^{o}C$ and 50% R.H. before testing.

Figure 51 shows the effect of re-extrusion on the weatherability of ultraviolet stabilized Dow polypropylene. The results show no significant change in property retention after seven extrusions.

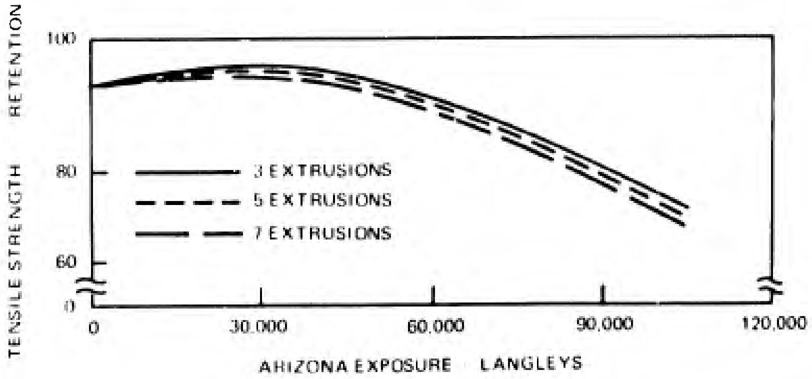


Figure 51. Effect of re-extrusion on outdoor stability of Dow polypropylene natural samples (43)

Figures 52 and 53 compare the effect of 1 percent TiO_2 pigment on the outdoor and accelerated weathering of polypropylene. The presence of titanium dioxide (as previously discussed) has a marked effect on the degradation of the samples. This is especially evident with the Florida exposure. Figure 54 shows the effect of a new ultraviolet stabilizer on the natural and pigmented systems after exposure in Arizona. (43)

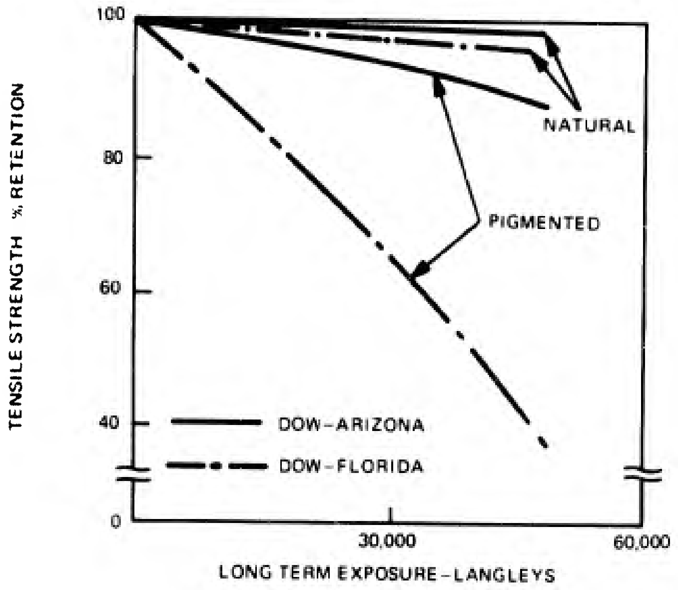


Figure 52. Florida vs. Arizona exposure of 10 mil monofilament natural and pigmented (1% TiO_2) samples (43)

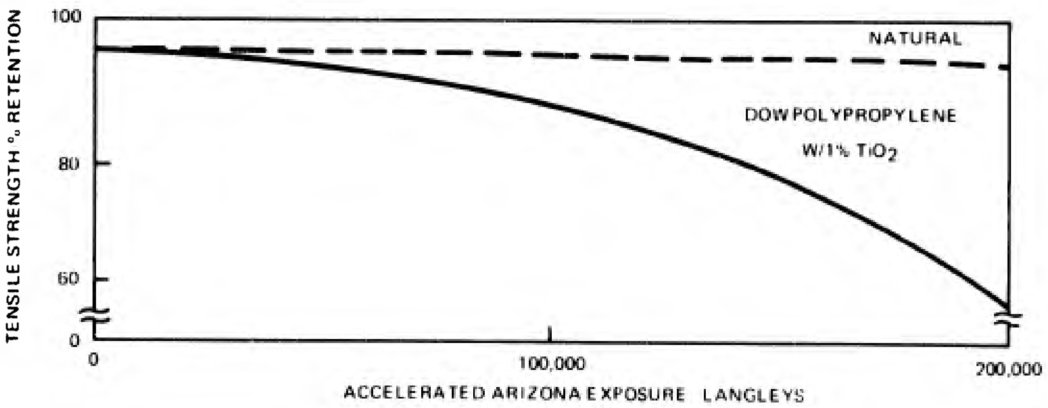


Figure 53. Accelerated Arizona exposure of natural and (1% of TiO_2) pigmented 10 mil monofilaments (43)

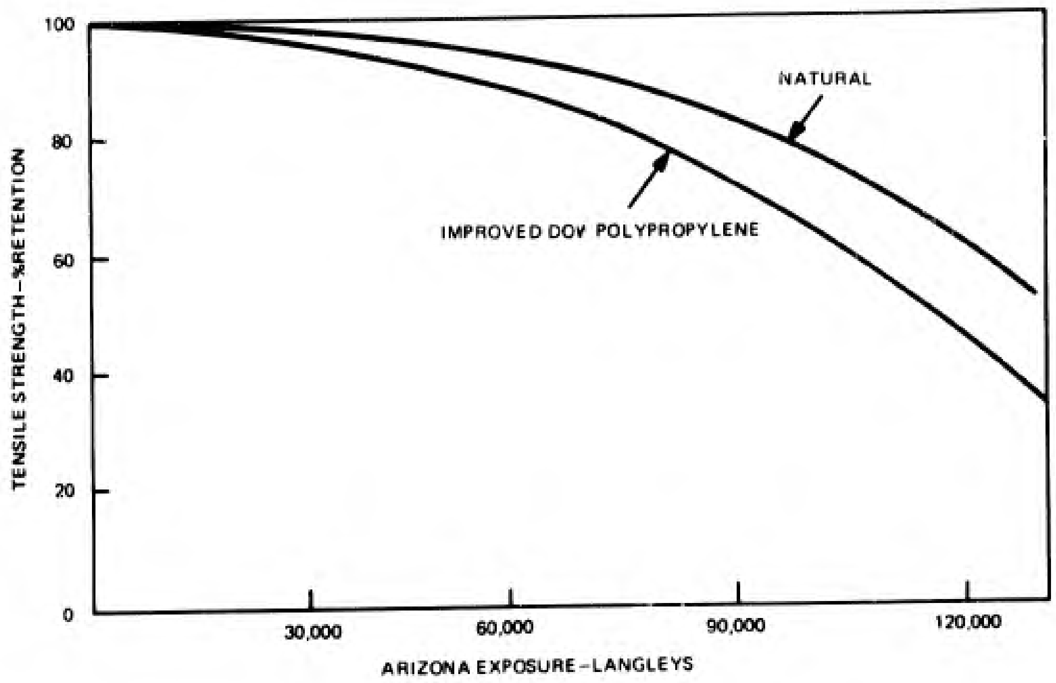


Figure 54. Arizona exposure of improved natural and pigmented (1% TiO_2) formulations (43)

SECTION VII. APPLICATIONS - CASE HISTORIES

It is interesting to note what developments have and/or are being made as a result of the growth of technology in weather resistance of plastics. According to Table 45, approximately 24.7 percent (or one quarter of all plastics produced) are expected to be exposed to weather in 1967.

Although this table reflects all plastics (not just polyolefins) it does indicate the significance of weather resistant plastics in the overall market. The overall market production for polyolefins in 1967 is estimated at 4.4 billion pounds. (45)

Before some specific end item applications of polyolefins are given, it is important to be cognizant of some factors besides formulation and geographical location, which can affect the life expectancy of an item.

- Item thickness - As previously stated, films will be affected by photo-oxidation much more than injection molded items since maximum absorption occurs at the surface of plastics containing uniform distribution of absorbing groups.

TABLE 45. INFORMATION ON THE PART OF U.S.'s 14.68 BILLION POUNDS OF PLASTICS SUBJECTED TO THE WEATHER
(1967 estimates) (13)

Market	Subjected to Weather		Total plastics consumption	Percent of its market
	Billions of pounds	Percent of total plastics		
Building & Construction	1.2	8.2	3.9	31
Packaging & Container	0.6	4.1	2.8	21
Electronics	0.3	2.0	1.9	16
Transportation	0.3	2.0	1.0	30
Pipe	0.3	2.0	0.5	60
Agriculture	0.03	0.2	0.03	100
Others (Military, etc.)	0.9	6.2	4.55	20
Total	3.63	24.7	14.68	24.7

Usage is classified only once under major market.

- Stresses - The presence or absence of stresses can influence the outdoor life of an item. Stresses can greatly accelerate the effects of weathering.

- Exposure requirements - The extent of outdoor use, whether intermittent or continuous outdoor use will greatly affect the life expectancy of an item. An item exposed two to three hours a week, for example, will certainly outlast the same material which is exposed continuously for several years.

The subject of outdoor applications for polyolefins could entail a report by itself. Therefore, only a few examples from literature will be given here to acquaint the reader with the various types of applications and the results obtained.

- Communications - Huge quantities of polyethylene are being used for sheathing and insulating billions of feet of conductor cable. Without carbon black and antioxidants, this sheathing and insulation would degrade seriously in less than twelve months. However, with the inclusion of these additives, deterioration has been arrested for years. The Bell Telephone System has had polyethylene cable sheathing in outdoor service for periods up to 20 years without any problems, 30 to 40-year life spans are anticipated. (44)

- Construction - A successful outdoor application of high density polyethylene is in stadium seats. In 1963, 6226 injection molded seats with a nominal thickness of 180 mils were installed at Our Lady of Snows Shrine in Belleville, Illinois, with both pigments and ultraviolet absorbers for protection. They have been in service for four years without failure or signs of visible degradation. Since then, both injection molded and blow molded seats have been installed in several stadiums including the Los Angeles Coliseum (two years), the San Diego Stadium and the Oakland-Alameda Stadium, with excellent weatherability. Weather-Ometer data on some of these formulations indicated that they should last a minimum of six years. (44, 12)

- Green polyethylene (density .960 melt index 0.2) cooling tower side panels (100 - 125 mils thick) have been in service in Bartlesville, Oklahoma for nine years without visible defects. Recent tests gave a tensile strength of 3,900 psi and absolute elongation of 13 percent. Weather-Ometer data on the same formula only 60 mils thick is shown in figure 55. (12)

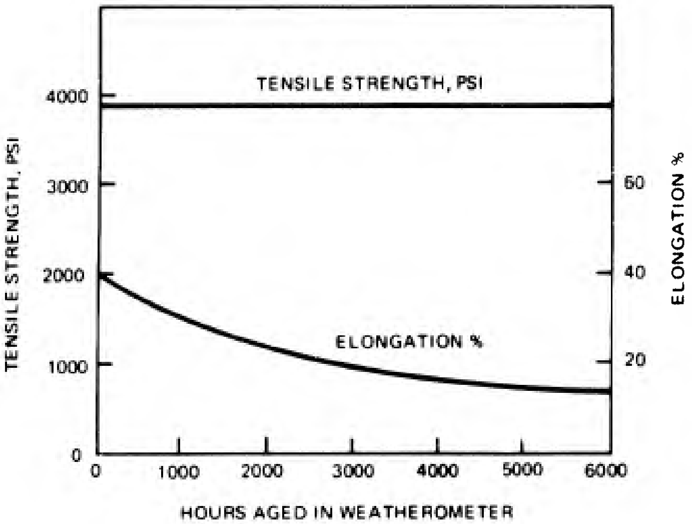


Figure 55. Effect of weathering of cooling tower side panels (12)

- Red and green decorative polyethylene fencing material has been in service in Bartlesville, Oklahoma for six years. The tensile strength and elongation are reported at 5000 psi and 14 percent for the red, and 4800 psi and 13 percent for the green after 6 years exposure. (12)

- Miscellaneous - High density polyethylene newspaper delivery tubes have been exposed since 1959 throughout the country. The Newspaper Enterprise Association reported no deterioration in tensile strength, color or surface from exposure. (44)

- Low density polyethylene trash cans have been improved to eliminate stress-cracking. Today a line of bins in eight sizes and various colors have been reported to withstand direct exposure in Texas without harmful effects. (44)

- A yellow polyethylene traffic marker guide stabilized with phenyl salicylate has been in service over seven years in Oklahoma. However, there was some surface crazing and loss in the original color. (12)

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The "Weatherability of Polyolefins" is the first of a series of reports on the weather resistance of non-reinforced plastics. It covers the effects of the weathering components on polyolefins; exposure testing methods; means of stabilization and the effects of pigments. In addition, a few examples of successful polyolefin outdoor applications are given.

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