

## THE PHILOSOPHY AND PRACTICE OF DEGRADABLE PLASTICS

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### ABSTRACT

A major advantage of plastics in packaging is their resistance to attack of microorganisms. After discard, however, this characteristic creates major problems in their disposal, since unlike nature's litter, they do not return to the biological cycle. Strategies for retaining the advantages of plastics during use but of triggering biodegradation after discard are discussed. Photobiodegradable plastics which have been used successfully as agricultural mulching film for many years are seen to be the potential solution to the marine debris problem.

### THE ENVIRONMENTAL IMPACT OF PLASTICS

The growth of consumer packaging has been one of the most visible phenomena of the twentieth century. On balance, it has been a beneficial development which has facilitated the distribution and storage of perishable goods to the advantage of the international community.

The modern packaging industry has its roots in the petrochemical industry, and the cheap commodity plastics, polyethylene, polypropylene, polystyrene, and polyvinyl chloride, are the major polymeric materials currently in use. They have a number of advantages in common, of which the following are the more important:

- They are cheap and easy to fabricate into common items of packaging.
- They are resistant to water and microorganisms and are, therefore, able to protect perishable goods from biological attack.

However, the very characteristics which make plastics so useful in packaging cause considerable problems in their ultimate disposal. Unlike cellulosic packaging materials (paper, cardboards, and the cellulose-based plastics), the oil-based plastics do not biodegrade back to the carbon

cycle when discarded in the environment. This is why they present one of the most visible litter problems of the twentieth century. The persistence of plastics litter in recreational areas, where it gave maximum offense, became evident in the late 1960's. The response of the plastics industry at that time was to say that it was unlikely that technical solutions to this problem could be found because the characteristics of biodegradable plastics were "the antithesis of the nature of packaging materials" (Staudinger 1970). The Society of Chemical Industry in 1970 expressed its alternative strategy as follows:

" . . .the Society will seek to make common cause with all movements and organisations concerned with preventing environmental deriliction [sic] by littering" (Staudinger 1970).

This did not mean that they would encourage research into making plastics more biocompatible, but that they would encourage educational programs directed toward making the public more environmentally aware of the litter problem. This is still essentially the polymer industry's public stance today. The responsibility for plastics pollution is presented as that of the user, who must be educated into nonlittering habits (Claus 1987; O'Connell 1987; Society of the Plastics Industry 1988).

In the meantime, the problem continues to grow. There was a temporary respite in the mid-1970's, when it appeared that the oil crisis would lead to widespread recycling of plastics waste. This did not happen on any scale for technical and sociological reasons, and the problem became more severe even through the years of high polymer prices.

One of the earliest surveys of plastics pollution in the seas was carried out by the author in the early 1970's. Over a 3-year period, a fivefold increase in plastics litter was observed on a remote shoreline in northwest Scotland (Table 1) (Scott 1972a, 1975a). The conclusion drawn from this survey was that most of the plastic litter found on the seashore is seaborne and wind driven. The nature and location of the litter suggested that it came predominantly from shipping and not from local inhabitants or visitors. In this context, the good intentions of the educators were seen to be both misguided and misdirected. Commercial pressures to use the sea as a convenient "waste bin" have proved to be much more persuasive than homilies by The Tidy Britain Group, and even the threat of legislation has little effect due to the difficulty of policing this on the high seas.

This early evidence of sea littering has been confirmed by many subsequent studies (Dixon and Cooke 1977; Dixon 1978; Dixon and Dixon 1981; Fowler and Merrell 1986; Andrady 1987; Heneman 1988), and there is increasing evidence that plastics debris can kill birds and animals by ingestion and strangulation (Fowler and Merrell 1986; Andrady 1987; Heneman 1988).

Certain types of nonbiodegradable plastics waste have come in for most criticism over the years. The most visual and intrusive are the large polyethylene bags used for packaging agricultural and industrial products and domestic carrier bags, all of which float on the sea and accumulate on land. Even more aesthetically objectionable are the smaller items which

Table 1.--Accumulation of plastic litter at Strathaird Point, Isle of Skye, Scotland, in a 3-year period (number of packages per 50 yd).

Type of packaging (polymer) <sup>a</sup>	August 1971	August 1974
Detergent (LDPE)	7	5
Detergent (HDPE)	--	31
Bleach, sanitary fluid (HDPE)	15	49
Oil (HDPE)	4	18
Cosmetic (HDPE)	3	3
Carpet cleaner (HDPE)	--	5
Food (HIPS or ABS)	1	7
Table salt (HDPE)	--	10
Milk (HDPE)	--	16
Heavy gauge bags (LDPE)	2	6
Small transparent bags (LDPE)	--	29
Carrier bags (LDPE)	--	5
Heavy gauge sheets (LDPE)	6	15
Miscellaneous unidentified	3	14

<sup>a</sup>LDPE - low density polyethylene, HDPE - high density polyethylene, HIPS - high impact polystyrene, ABS - acrylonitrile-butadiene-styrene copolymer.

originate from sewage disposal and which, although probably harmless compared with other components of sewage, cause great offense on beaches and in other environmentally sensitive areas (Johnson 1987). Six-pack collars, used for carrying beer and soft drink cans, have been particularly indicted as a cause of entanglement for birds and small animals, and discarded ropes and fishing nets are equally a cause of suffering and sometimes death to wildlife. These are all examples of litter which does not biodegrade, and although the polymers do degrade slowly under the influence of sunlight and oxygen and the erosive influence of the weather, these natural processes are not fast enough to eliminate the dangerous effects of man-made polymers in the environment.

Fortunately, a good deal of work in academic laboratories, particularly in the United Kingdom and Canada, had led to an understanding of the chemistry involved in the oxidative degradation of polymers. Associated with this was a fundamental understanding of antioxidant and ultraviolet (UV) stabilizer mechanisms which suggested the possibility of designing polymers with controlled outdoor stability.

## THE ENVIRONMENTAL STABILITY OF POLYMERS

### Biodegradability of Polymers

As has been discussed above, the main reason that the man-made polymers have assumed a position of such importance in the packaging

industry is because of their excellent water barrier properties. Since they are not readily penetrated by water, they act as an effective barrier, even in very thin films, to the attack of microorganisms. However, just because they are not accessible to microorganisms, they normally remain resistant to microbiological attack after discard in the environment.

All man-made polymers are not so hydrophobic as the carbon-chain polymers, however, and in general, the closer in structure polymers are to the natural polymers, the more biodegradable they become. Thus, the polyamides, which resemble the polypeptides in chemical structure, do absorb water and slowly biodegrade. In the case of polyurethane foams, biodegradation may take place quite rapidly because of the high internal surface area of the foam structure. Recently, man has been able to utilize nature's ability to synthesize and store within the biological cell certain types of polyester (Table 2) to produce a truly biodegradable polymer with physical and mechanical resemblances to the polyolefins (Lloyd 1987).

It is an unfortunate irony, however, that the nearer synthetic polymers approach the structure and properties of the natural polymers, the less useful they become as packaging materials because of the impairment of their barrier properties. Cellulose-based packaging has been largely abandoned over the years in favor of the hydrophobic polymers, and it is highly unlikely that the packaging industry would now be willing to return to less effective materials even if they could be produced at the same price as commodity plastics. It appears then that some other stratagem has to be sought to ensure that packaging materials are returned to the biological cycle when discarded in the outdoor environment.

#### Oxidative Degradation of Polymers

All organic polymers degrade due to the combined effects of oxygen, sunlight, and water by processes which do not, at least in the early stages, involve biological agencies (Scott 1965). They do so, however, at rates which differ by several orders of magnitude. Fluorinated polymers (e.g., Teflon) are in general the most resistant to environmental deterioration, and in the absence of light they can survive for many decades. Hydrocarbon polymers, and particularly the unsaturated rubbers, are much less resistant to oxidation, and even polyethylene, which on the basis of its structure should be chemically inert, does oxidize slowly unless protected against the effects of the environment. The small amounts of antioxidants which are added as processing stabilizers are normally sufficient to effectively stabilize polyethylene against the effects of oxidation in the absence of sunlight, but much more effective combinations of antioxidants and light stabilizers have to be used in order to give the polymer the durability required for use in outdoor applications (Scott 1979-88; Grassie and Scott 1985).

Oxidation of polymers leads to the formation of a variety of oxygen-containing functional groups as part of the polymer chain, of which the most important are hydroperoxides, carbonyl groups, alcohols, and carboxylic acids (Fig. 1) (Grassie and Scott 1985). These lead to the modification of the polymer surface, making it hydrophilic and allowing microorganisms to preferentially remove the oxygen functions. Figure 2

Table 2.--Commercially available degradable plastics.

Common description	Composition	Trade name	Manufacturer
<b>Biodegradable polymers</b>			
Poly (3-hydroxybutyrate-3-hydroxyvalerate)	Biosynthetic copolymer of 3-hydroxybutyric and 3-hydroxyvaleric acids	Biopol	ICI (United Kingdom)
<b>Polymers containing a biodegradable filler<sup>a</sup></b>			
Starch-filled polyethylene (Griffin process)	Physical blend of LDPE and starch	Bioplast Ecostar	Coloroll (United Kingdom) St. Lawrence Starch (Canada)
<b>Photodegradable copolymers</b>			
Ethylene-carbon monoxide copolymers		E/CO	DuPont (United States) Union Carbide (United States) Dow (United States)
Vinyl ketone copolymers (Guillet process)	Copolymers of ethylene, propylene, and styrene with a vinyl ketone	Ecolyte	EcoPlastics (Canada)
<b>Photosensitizing and photoactivating additives</b>			
Iron salts	Probably ferric stearate	PolyGrade	Ampercet (United States)
Aromatic ketones	Probably benzophenone with metal stearates	Not commercial	Princeton Polymer Lab. (United States)
Antioxidant photoactivator (Scott-Gilead process)	Ferric thiolates (sometimes with other metal thiolates (in polyethylene)  (in polypropylene baler twine)	Plastor Greenplast Plastigone Ecoten <sup>b</sup> Litterless Cleanfield	Plastopil (Israel) Polydress (Germany) Enichem Agricoltura (Italy) Plastigone Technologies Inc. (United States) Amerplast (Finland) Plastigone Technologies Inc. (United States) American Brazilian Company (United States)

<sup>a</sup>LDPE = low density polyethylene. <sup>b</sup>Manufacture discontinued.

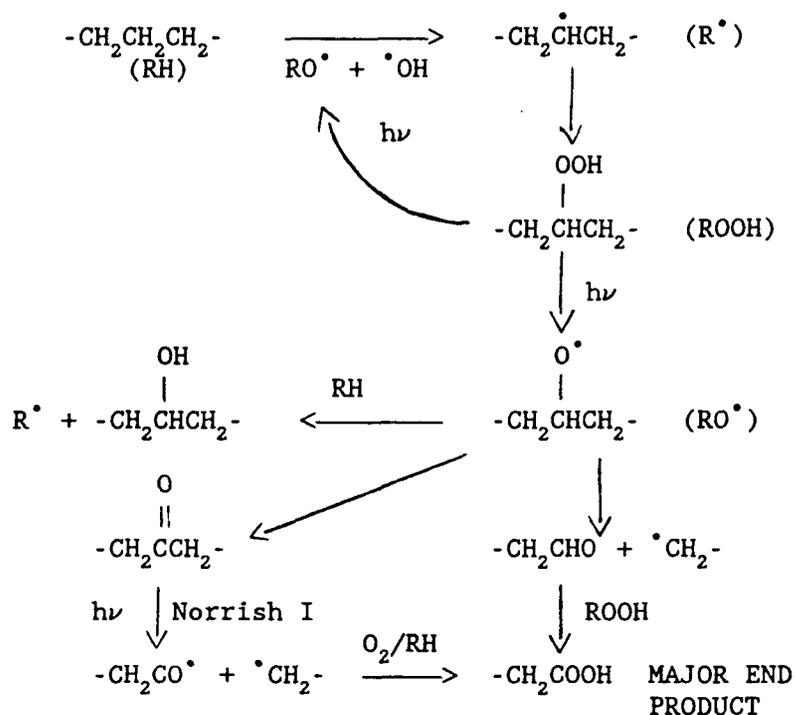


Figure 1.--Products formed in the photooxidation of polyethylene.

shows that polyethylene, stored under ambient conditions, develops a substantial concentration of carbonyl compounds ( $1,710\text{-}1,735\text{ cm}^{-1}$ ), and that these can be selectively removed by microorganisms, leaving a chemically "purer" polymer behind (Grassie and Scott 1985).

Deliberate preoxidation of polyolefins leads to an enhanced rate of attack of thermophilic fungi at  $40^\circ\text{-}45^\circ\text{C}$  due to the formation of readily assimilable dicarboxylic acids (Eggs et al. 1971). Some plasticizers also accelerate this process, probably in part by accelerating the autoxidation of the polymer (Eggs et al. 1971). Recently, the addition of oxidizable oils (e.g., soybean oil) to polyethylene has been used to accelerate the rate of thermal oxidation of starch-filled polyethylene in compost at elevated temperatures in order to make the starch available to microbiological attack (Griffin 1987; Maddovar and Chapman 1987). The rationale behind this approach to biodegradable polyethylene is not entirely clear, since the starch is encapsulated in biologically resistant polymer which does not oxidize at a significant rate at ambient temperatures. Moreover, the process cannot occur in landfill because no oxygen is present and the unoxidized polymer backbone cannot be assimilated by microorganisms (Potts 1982).

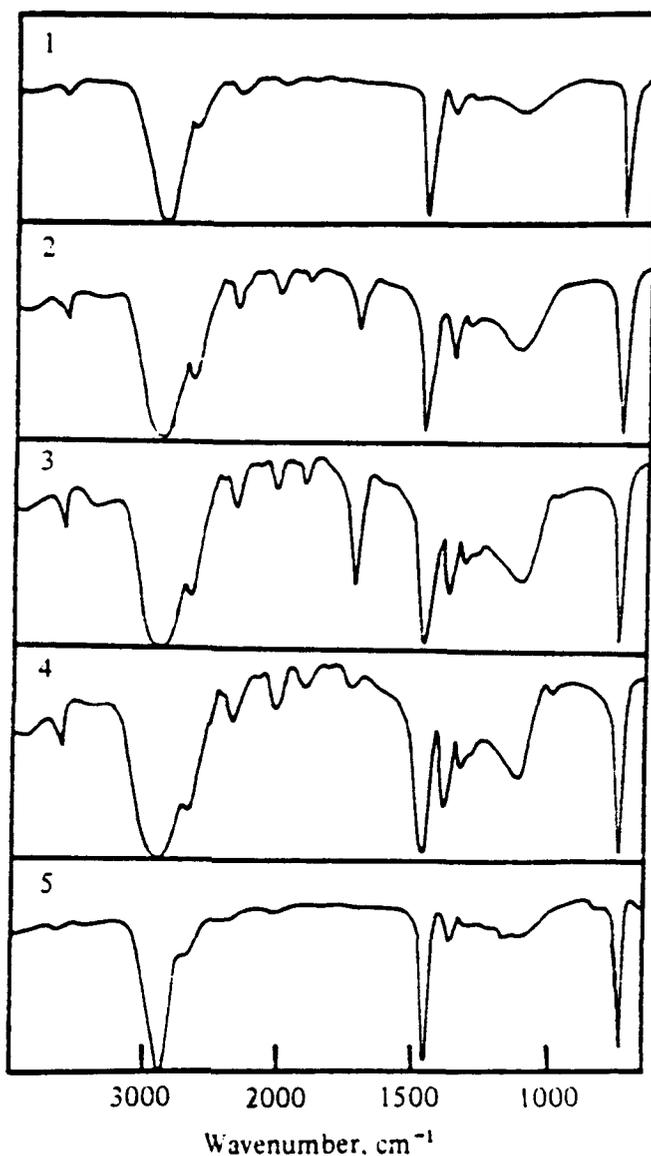


Figure 2.--Infrared spectra of high density polyethylene (HDPE) films with different histories: 1--with antioxidant after standing at ambient temperature for 1 year; 2--as 1 without antioxidant; 3--as 2 after standing for 3 years; 4--as 3 after treatment with an aerated medium inoculated with cultivated soil; 5--HDPE powder without antioxidant exposed to aerobic biodegradation for 2 years before molding to film with exclusion of air. (Grassie and Scott (1985) with permission, originally reproduced from a doctoral thesis by Dr. A. C. Albertsson with permission.)

### Photooxidation of Polymers

Thermal oxidation of polymers is not a very controllable process. Although it can be catalyzed by cooxidation agents or transition metal ions, these are present in varying amounts of foodstuffs. However, autoxidation is readily inhibited by antioxidants, which are deliberately added to stabilize the polymer during manufacture (Grassie and Scott 1985). Furthermore, the addition of even a few percent of polymer-soluble coagents substantially alters the physical characteristics of the polyolefins (Scott 1988a, 1988b).

Photooxidation, by contrast, is a much more controllable process, since it is not appreciably affected by thermal antioxidants or contaminants. As early as 1971, it was suggested (Eggins et al. 1971) that controlled photooxidation was a potentially useful way of dealing with the problem of nonbiodegradable packaging litter. It offers the very considerable advantage over true biodegradation of the main polymer chain that, until photooxidation has occurred in the environment where the package has been discarded, its properties do not differ in any respect from conventional packaging made from the same polymer. The mechanism of photooxidation is essentially similar to that of thermal oxidation. The essential difference is the way in which the autoxidation chain reaction is initiated, which, in turn, depends on the presence of photoinitiators in the polymer (Grassie and Scott 1985).

Typical photoinitiators that have been used to sensitize the photodegradation of plastics in the outdoor environment after discard are listed in Table 2. Although many more have been reported in the patent literature, these are the only ones which have reached the marketplace. Companies producing them are also listed in Table 2.

Photodegradable plastics can be broadly classified into types:

- Copolymers in which the sensitizer, a carbonyl group, is built into the polymer.
- Conventional plastics to which the sensitizer is added, generally as a masterbatch and in some cases as a replacement for the usual processing stabilizer.

#### Copolymers

In the first approach, degradation occurs primarily by photolysis of the polymer backbone, leading to reduction in molecular weight and fragmentation of the polymer (Fig. 3). The Norrish Type II process is the predominant mechanism leading to chain scission, giving rise to ketone and vinyl groups at the end of the polymer chains (Grassie and Scott 1985). An early example of such a carbonyl-modified polymer was claimed in a patent by DuPont (Brubaker 1950), and this process has been commercialized relatively recently by DuPont and Union Carbide among others (Johnson 1987). The polymers embrittle rapidly and without any induction period (Harlen and Nicholas 1987; Statz and Dorris 1987), and if a period of

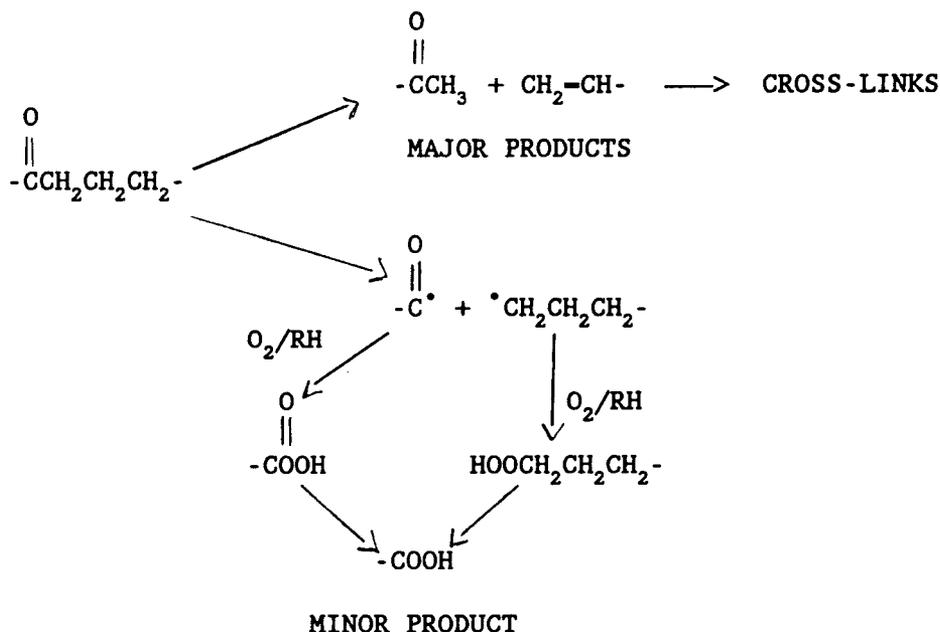


Figure 3.--Photolysis of in-chain carbonyl in polyethylene.

"safe" use is required, for example in storage or for a defined period out-of-doors, then the packaging has to be protected against UV irradiation. This kind of degradable plastic cannot, therefore, be used in agricultural protective film (mulch), where the polymer has to retain its strength for a well-defined period of time in sunlight but then has to photodegrade rapidly over a period of a few weeks. Rapid degradation appears to cease after all the in-chain carbonyl groups have photolyzed, and there is evidence (Harlen and Nicholas 1987) that the molecular weight decreases to a minimum and then increases again (Table 3). There is a similar minimum in the elongation to break, and these phenomena suggest that oxidation does not occur to any extent. This is consistent with the fact that if biodegradation does occur, it is extremely slow (Statz and Dorris 1987)--a considerable disadvantage of this type of product, since the fragmented products will still tend to accumulate in the environment.

In a more sophisticated approach to photodegradable copolymers, Guillet and his coworkers have copolymerized a variety of monomers, of which styrene, ethylene, and propylene are the most important, with vinyl ketones (Guillet 1973). These polymers have been commercialized under the name Ecolyte by Ecoplastics Ltd. (Redpath 1987). These polymers photolyze by essentially the same mechanism as the E/CO polymers, but both Guillet (Guillet et al. 1974; Jones et al. 1974) and Redpath (1987) have reported that the Ecolyte copolymers do biodegrade after fragmentation. This implies that the Norrish Type I process must play some part in initiating a conventional autoxidation chain reaction. However, the Ecolyte polymers suffer from the same disadvantage as the E/CO polymers in that they do not

Table 3.--Molecular weight changes in E/CO polymer (2.74% CO) on ultraviolet irradiation.

Exposure time, h	$M_n$	$M_w$
0	45,000	618,700
650	7,300	15,000
1,350	11,100	39,100

have a controllable induction period before rapid photodegradation commences.

#### Sensitizer Additives

In this approach, two main types of additive have been used. The first class falls broadly into the general class of triplet sensitizers, most importantly the benzophenones (Takahachi and Suzuki 1964) (see H. Omichi (1983) for a survey of the literature up to 1983). The mechanism of their action is summarized in Figure 4 and the related quinones act in the same way. Although the carbonyl sensitizers cause rapid photooxidation from the beginning of UV exposure, they autoretard rapidly in the case of

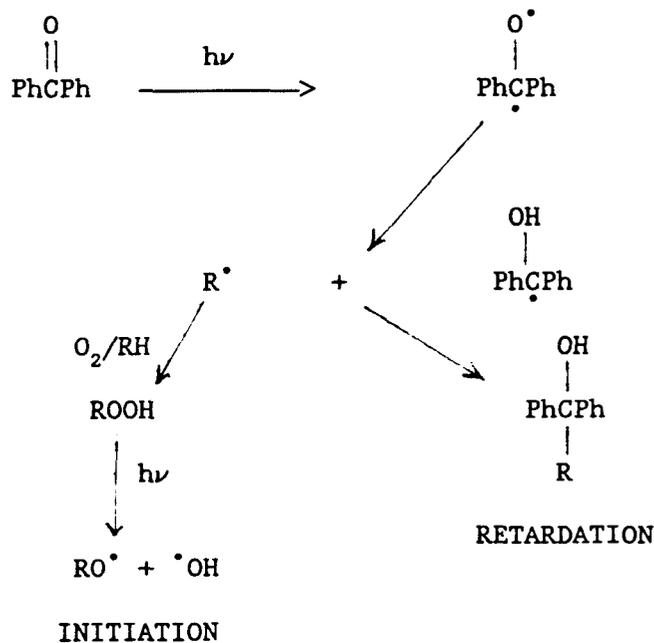


Figure 4.--Mechanism of photoinitiation and autoretardation by triplet sensitizers.

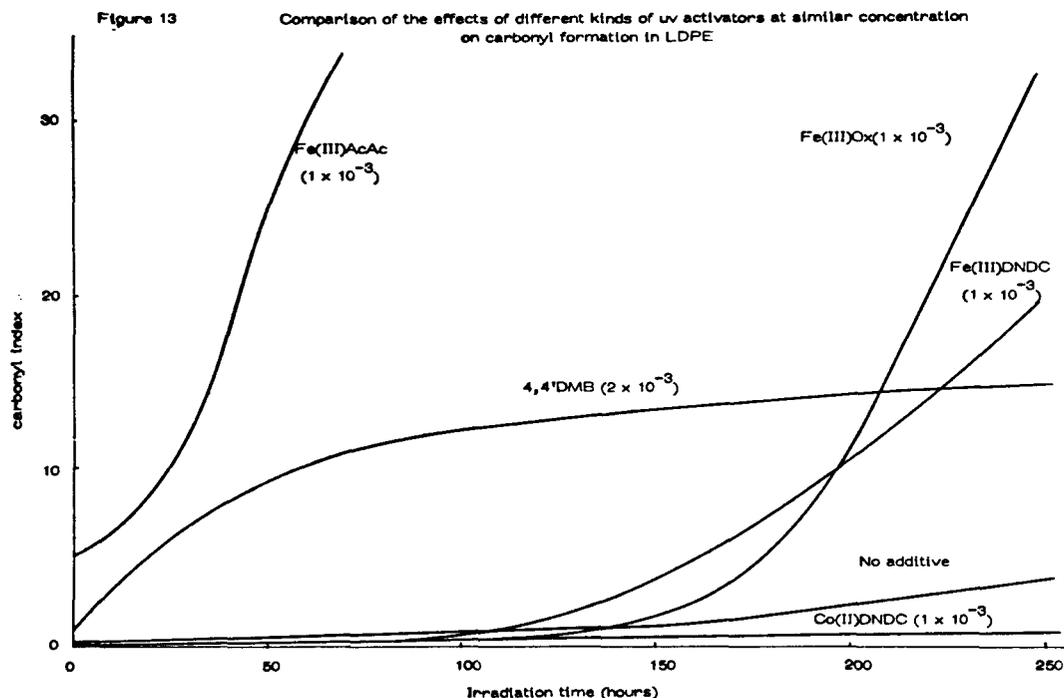


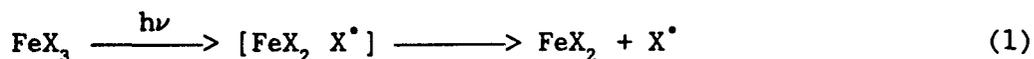
Figure 5.--Comparison of the photooxidation, as measured by carbonyl formation (at  $1,710\text{ cm}^{-1}$ ), of low density polyethylene (LDPE) films containing different kinds of photoactivator at similar concentrations. 4,4'DMB, 4,4'dimethoxybenzophenone; Fe(III)AcAc, iron acetyl acetonate; Fe(III)DNDC, iron dinonyl dithiocarbamate; Fe(III)L2, iron complex of 4-methyl-2-hydroxyacetophenone oxime; Co(II)DNDC, cobalt dinonyl dithiocarbamate (UV stabilizer). (From Amin and Scott (1974) with permission.)

polyethylene and the photooxidation virtually ceases after a period of time (Fig. 5) (Takahachi and Suzuki 1964). This is because the hydrogen abstraction step in Figure 4 leads to a "stable" radical which is able to trap out the chain-carrying species formed in the photooxidation process. This has unfortunate consequences for the long-term oxidation and biodegradation of the polymer, and this, coupled with the lack of an appropriate time control mechanism, has resulted in no commercial developments with this type of sensitizer system.

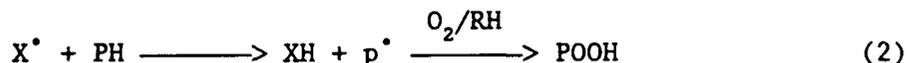
The second class of photosensitizer additives is based on transition metal ion compounds and is the most important class in use today. Transition metal ions have been extensively studied as photosensitizers for polyolefins (Takahachi and Suzuki 1964; Mellor et al. 1973; Amin and Scott 1974; Chew et al. 1977). Many polymer-soluble metal carboxylates, notably  $\text{Co}^{3+}$  and  $\text{Fe}^{3+}$ , are powerful photoprooxidants which catalyze

photooxidation right from the beginning of UV irradiation (Fig. 5), and in the form of polymer-soluble carboxylates or acetylacetonates they cause melt degradation of the polymer during processing (Amin and Scott 1974). They cannot, therefore, be used alone in polymers in conventional processing operations because of their unfortunate effect on the melt stability of polymer and on the shelf-aging behavior of the fabricated product. Although conventional antioxidants improve processing and aging characteristics, they also interfere with the photosensitizing effect of the transition metal ions (Mellor et al. 1973).

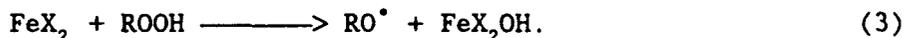
The photoinitiating mechanism of the transition metal salts involves photolysis to give the reduced form of the metal ion and a free radical:



The anion radical readily abstracts a hydrogen atom from the polymer

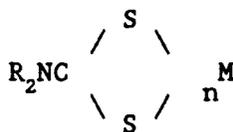


Once formed, hydroperoxides control the subsequent oxidative degradation by the usual redox reactions with metal ions, e.g.,

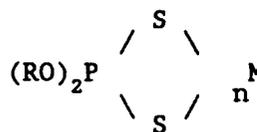


#### Transition Metal Ion Antioxidant-Photosensitizers

Many metal complexes containing sulphur as a ligand are antioxidants and photostabilizers. Although this behavior is not limited to sulphur compounds, members of the latter class have gained a position of some importance as heat and light stabilizers for polyolefins (Scott 1965; Al-Malaika et al. 1983; Al-Malaika and Scott 1983). The dithiocarbamates (I) and the dithiophosphates (II) are representative of this class of stabilizers and exert their effect by destroying hydroperoxides by an



I



II

ionic mechanism (Al-Malaika et al. 1983; Al-Malaika and Scott 1983). One of their most striking and useful attributes is that they produce a well-defined and reproducible induction period during which the ligand is destroyed and at the end of which the metal ions which form part of the antioxidant are released and subsequently behave very much like the free transition metal ions described in the previous section (Fig. 5) (Scott 1965).

In 1971, Scott filed a patent based on the above concept in which antioxidant and photosensitizer properties were both contained in the same molecule, although this could be made in situ in the polymer by reacting the metal ion with the antioxidant (Scott 1971). The Fe(III) complexes of I and II are representative of this class of "delayed action" photoactivators. Not only do they replace conventional processing stabilizers by virtue of their antioxidant properties, but they are also effective heat stabilizers and short-term light stabilizers. The fact that the induction period to photooxidation could be controlled by varying the concentration of the metal complexes led in the early 1970's to the use of this system in agricultural mulching film, which requires a finely controlled lifetime before rapid photooxidation and biodegradation commences (Scott 1972b, 1972c, 1973a, 1973b, 1973c, 1975b, 1975c, 1976; Scott and Gilead 1978). This material was marketed as Plastor by Plastopil Hazorea, and subsequent development in collaboration with Gilead led to further patents (Scott and Gilead 1978) concerned with the fine control of the "safe" period, which is so essential for agricultural purposes (Scott and Gilead 1982).

The later developments involve the use of two component systems in which the length of the induction period is controlled by one metal thiolate and the rate of photooxidation by a second. The Scott-Gilead process is currently used in the commercial growing of soft fruits, vegetables, and some cereals in Italy, Germany, France, and the United States. In addition to the name Plastor, these products are sold under the trade names Greenplast (Enichem Agricoltura, Italy), Plastigone and Litterless (Plastigone Technologies Inc., United States). The process is also used in polypropylene binder twine by the American Brazilian Company in the United States under the trade name Cleanfield.

The use of the Scott-Gilead system in agriculture has established the reliability of this technology. Figure 6 shows it in use near the Dead Sea in Israel. At the end of the induction period, the polyethylene film photodegrades rapidly, and biodegradation is complete by the beginning of the following season. There has been no buildup of nonbiodegraded plastics on any of the sites where it has been used.

In parallel with the above developments, trials began on the use of the original iron thiolate system in packaging. This led to the manufacture of carrier bags in Finland in 1973 under the name Ecoten. Figures 7 and 8 illustrate the progression of the degradation of Ecoten carrier bags exposed at intervals out-of-doors in Birmingham (Scott 1976). The time delay of about 2 weeks of summer sunshine before rapid degradation commenced was introduced at the request of the user to safeguard against adventitious exposure to light of the packaging during use. A measure of the effectiveness of the iron thiolates as thermal antioxidants is the fact that 15 years after their manufacture, carrier bags made by this process and stored in the absence of light are still as strong as when they were first manufactured. This process is currently being evaluated in check-out bags (United States), carrier bags (United Kingdom), and six-pack collars (United States), all of which tend to end up as litter.



Figure 6.--Progress of photooxidation and biodegradation of Plastor (photobiodegradable) mulching film in Israel. 1--immediately after laying; 2--after cropping; 3--after ploughing. (Photographs by courtesy Plastopil Hazorea, Ltd.)



Figure 7.--Ecoten carrier bags exposed out-of-doors in Birmingham at 1-month intervals.

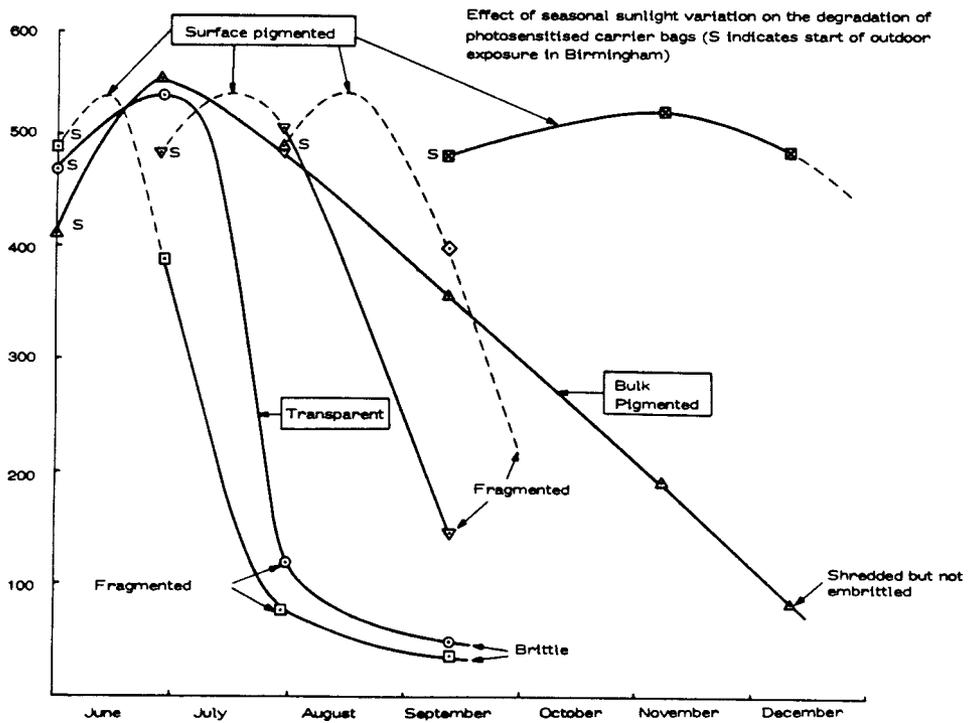


Figure 8.--Change in mechanical properties of Ecoten carrier bags exposed out-of-doors in Birmingham at 1-month intervals.

## TECHNICAL REQUIREMENTS OF PHOTOBIODEGRADABLE PLASTICS

In spite of the successful use of photobiodegradable plastics in agriculture and to a lesser extent in packaging over the past 15 years, the packaging industry has been reluctant to accept them as a contribution toward the control of plastics litter. The arguments used against them are frequently couched in technical language, but are very often based on misconception rather than on technical fact and experience. The critics of degradable plastics are generally governed less by the published scientific evidence than by a reluctance to accept liability for the pollution resulting from the activities of their own industry. The pseudosociological arguments frequently used are intended as much for politicians as for the users of packaging.

The use of degradable plastics in agriculture was dictated by economic necessity. The same pressures are not evident in the use of degradable plastic in packaging, since rapid disintegration after use does not enhance the primary function of the package. Legislative bodies have, therefore, been reluctant to prohibit the use of nondegradable materials for purely aesthetic reasons. However, it is now clear that the situation is much more critical in the oceans, where there is a real threat to marine birds and animals. Experience in agriculture has unambiguously demonstrated that there are no economic or technical reasons why photobiodegradable plastics should not now be introduced into all bulk packaging. There is increasing evidence that the manufacturers and users of packaging are beginning to listen to the "green" movements, which advocate working with rather than against nature. The idea of returning waste plastics to the biological cycle is rapidly gaining popularity with the retailers of "organic" products and even with the large supermarkets.

However, packaging manufacturers are faced with a dilemma. The claims of the various degradation systems available are very difficult to check out. Furthermore, where they have been evaluated, the performance of some of the processes does not match up to the claims made for them. The terminology used is often confusing, and most technologists cannot distinguish between the subtleties of anaerobic and aerobic biodegradation, photodegradation, and photobiodegradation. There are at present no objective performance tests currently available which allow the user to compare the performance of degradable plastics. Until such criteria are available, it seems likely that the polymer industries will continue to argue on specious grounds against the introduction of more biocompatible, but also potentially more expensive, materials. In these circumstances, it seems unlikely that the polymer industries themselves will wish to fund the necessary research to establish the appropriate standards. The pressure for change must come from the users of packaging in association with the environmental pressure groups.

## NET PACKAGING AND FISHING NETS

One of the most serious threats to marine life undoubtedly comes from ghost fishing, where both animals and fish become fatally entangled in

Table 4.--Combination effects of a photoactivator (FeDMC, 0.01 g/100 g) and a photostabilizer (NiDBC, variable) on the photooxidative stability of polypropylene.

Concentration of NiDBC, g/100 g	0	0.1	0.2	0.3	0.4
Embrittlement time, in hours	116	956	1,515	2,250	2,516

discarded nets. Much of this lethal debris arises accidentally by natural wear and tear on fishing gear, which has a finite life due to normal oxidative aging and biodegradation processes. Some of it, however, particularly in the packaging field, results from deliberate discard by the user. Most of the polymer used in these applications is polyolefin-based and so, as seen above, does not biodegrade rapidly unless sensitized to oxidation. An exceptionally wide range of lifetimes is thus required for netting, ranging from packaging, where ideally photobiodegradation should commence immediately on discard, to fishing net, where a service life of 5 years or more is required. This might at first sight appear to be an impossible achievement when coupled with the need for rapid photooxidation and biodegradation at the end of the useful life of the net. In practice, the Scott-Gilead system has been shown to be capable of providing this range of degradation times in polypropylene and high density polyethylene.

Table 4 shows that different combinations of photoactivator (FeDMC) and photoantioxidant (NiDBC) in polypropylene give a twenty-fivefold range of useful lifetimes (Scott and Gilead 1982), and more recent work has shown that this can be increased to a greater than fiftyfold range using a combination of different additives. In practice, this means that if a lifetime of 2 months is required for short-term packaging, then, using the same polymer but a different combination of the same additives, a lifetime of 8 years is technically feasible for fishing nets. This extraordinary lifetime control is accompanied in all cases by rapid photooxidation and biodegradation after embrittlement of the fiber. This process is already in commercial use in polypropylene binder twine (American Brazilian Company), where a lifetime of about 1 year is required followed by the rapid disappearance of the fiber from the field. It is fortunate that polypropylene, due to its low density, floats on the surface of water, where it is subjected to the combined effects of sunlight, oxygen, and microorganisms. This process is ideal for the protection of the environment from net packaging, ropes, and fishing nets which fail in service.

#### THE FUTURE

Polymer technologists have in the past been concerned to make sure that their products lasted as long as possible in the environment. It is increasingly being recognized that a more sophisticated approach is required in the future. Many products are required to last only as long as

they fulfill their useful function, and the chemistry of stabilization has now advanced to the point where predictable lifetime control of polymeric materials is not only feasible but is now well proven through the pioneering activities of Gilead and his coworkers in plasticulture (Scott and Gilead 1982; Gilead 1985; Gilead and Ennis 1987).

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