

Metal-Organic Stabilizers and Antistabilizers for Polyolefin Plastics

G. C. NEWLAND and J. W. TAMBLYN, *Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee*

Synopsis

During the past few years it has been reported that a number of metal-organic compounds show outstanding effectiveness as stabilizers against the oxidative deterioration of polyolefins and other polymers. This may seem surprising in view of the well known catalytic effect of such compounds on the oxidation of organic materials. Indeed, it has been observed that a given metal compound can act as a stabilizer in one system and as an antistabilizer in another. Even in a single system the compound may simultaneously retard one mode of oxidation and accelerate another. For example, the copper chelate of α, α' -(ethylenedinitrilo)-di-*o*-cresol retarded the formation of carbonyl groups and accelerated scission during the photooxidation of polyethylene. It is the purpose of this paper to consider a number of examples of this sort drawn from the field of metal-organic stabilizers.¹ Any comprehensive theory of oxidation and antioxidation should be able to encompass such curious anomalies.

Introduction

The use of various types of metal-organic compounds in polyolefin plastics for such things as polymerization catalysts, lubricants, and dyeing assistants has become a widespread practice in recent years. The effects of such additives on the overall stability of articles made from these plastics have not yet been thoroughly investigated. It is well known that many metal-organic compounds have high activities as catalysts for the oxidation of organic materials. For example, it has been shown at Bell Telephone Laboratories that copper (II) stearate is an extremely active catalyst for the oxidative deterioration of polypropylene at temperatures around 140°C.² On the other hand, a number of metal-organic compounds have recently come into prominence as highly effective stabilizers for polyolefins. For example, the nickel chelate of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol] has enjoyed considerable popularity as a stabilizer against the photooxidative and thermal oxidative breakdown of polyolefins.³

For the purposes of this paper, the term metal-organic compound has been used to include chelates and salts of metals with any organic compound.

A given metal-organic compound may exhibit a wide range of stabilizing or antistabilizing activity depending on the chemical nature of its environment and even on its concentration in a given environment. A very slight change in environmental conditions may cause the compound to act as either a stabilizer or antistabilizer. In the case of copper (II) stearate, it is reported that this compound, at a concentration of 0.08%, strongly catalyzed the oxidation of dibutyl sebacate and strongly inhibited the oxidation of diethyl phthalate at 150°C. under 1 atm. of oxygen.⁴ Russian workers reported that below a certain threshold concentration copper (II) stearate catalyzed the oxidation of decane and above this concentration inhibited the oxidation of decane.⁵

Results and Discussion

The performance of a good metal-organic antioxidant, zinc (II) dibutyldithiocarbamate,⁶ for polypropylene is shown in Table I. Typical phenolic, aromatic amine, and sulfur-containing antioxidants and a typical synergistic mixture of antioxidants are included in the table for comparison.

The additives listed in Table I were compounded with unstabilized polypropylene pellets in a Brabender Plastograph under an atmosphere of nitrogen at 190°C. for 5 min. The resulting mixture was granulated and injection-molded at 200°C. into tensile bars 2½ in. long × 1/16 in. thick, having a gauge section 1 in. long × 1/4 in. wide. These tensile bars were bent into a U-shape and inserted upside down into stainless steel channels, 5/8 in. wide × 1/2 in. deep. The channels containing the stressed tensile bars were placed in a mechanical convection oven at 140°C. and observed periodically for the appearance of cracks. The oven stress-crack life of a sample was defined as the heating time, in hours, required for the development of cracks visible to the unaided eye, in the stressed area.

As seen in Table I, zinc (II) dibutyldithiocarbamate prolongs the 140°C. stress-crack life of polypropylene to almost 4.5 times that obtained with the synergistic mixture. However, when the total concentrations were increased this ratio decreased.

TABLE I
Performance of Antioxidants in Polypropylene

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

^a Present in 0.1% concentration.

While the metal-organic compound, zinc (II) dibutyldithiocarbamate, is an effective stabilizer against thermal oxidation, a shift to an environment capable of inducing photooxidation diminishes its activity as a stabilizer. The performance of zinc (II) dibutyldithiocarbamate as an ultraviolet stabilizer is shown in Table II. A benzophenone-type ultraviolet stabilizer and a synergistic mixture⁷ of the benzophenone and the carbamate are shown for comparison.

The additives listed in Table II were incorporated into the polypropylene by slurring polypropylene powder with an acetone solution of the additives. After evaporation of the acetone, the polypropylene was compacted and injection-molded at 200°C. into tensile bars of the shape described previously. The tensile specimens were exposed in an Atlas Twin-Arc Weather-Ometer modified with ten 20-w. Westinghouse fluorescent sunlamps.⁸ The tensile specimens were removed after various lengths of exposure, and the percentage of elongation and the inherent viscosity were determined.

TABLE II
Performance of Ultraviolet Stabilizers in Polypropylene

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	1800	1050
{ 2-Hydroxy-4,4'-dimethoxybenzophenone	1		

The performance of zinc (II) dibutyldithiocarbamate as an ultraviolet stabilizer, or inhibitor of photooxidation, was rather poor, as demonstrated by the much greater efficiency of the benzophenone-type ultraviolet stabilizer. However, the synergism of the carbamate and benzophenone is clearly evident in the table. A comparison of the two methods, viscosity breakdown and loss of elongation, for evaluating the performance of the additive indicates that the zinc (II) dibutyldithiocarbamate is more effective in inhibiting viscosity breakdown than in inhibiting loss of elongation.

Work at Bell Telephone Laboratories has demonstrated the remarkable synergistic effect of certain sulfur-containing antioxidants on the heat stability of carbon black-pigmented polyethylene. Zinc (II) dibutyldithiocarbamate does not show this effect, despite its sulfur content. Its performance is contrasted in Table III with that of an effective synergistic sulfur-containing antioxidant, 4,4'-thiobis[6-*tert*-butyl-*m*-cresol].

TABLE III
Performance of Antioxidants in Black Polyethylene

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- <i>tert</i> -butyl- <i>m</i> -cresol]	0.1	65
{ Carbon black (Witco 100)	3	
{ Zinc (II) dibutyldithiocarbamate	0.1	42
{ Carbon black (Witco 100)	3	
{ 4,4'-Thiobis[6- <i>tert</i> -butyl- <i>m</i> -cresol]	0.1	>150

The compositions listed in Table III were prepared by hot-roll compounding, at a front and rear roll temperature of 240 and 210°F., respectively, polyethylene of melt index 20 with the additives to be tested. The roll slab, approximately 1/4 in. thick, was cut into six 0.25-g. samples, placed on a 20-mm. watch glass, and stored at 160°C. At intervals, one of these samples was removed and its peroxide content determined.⁶ The oven life was defined as the time, in hours, before peroxides were formed. The value was obtained by extrapolating the recorded peroxide data to zero peroxide content.

Anomalies in stabilizing behavior, similar to those described previously for zinc (II) dibutyldithiocarbamate, have been encountered with many other metal-organic compounds. Table IV shows the performances of some of these compounds as stabilizers against thermal oxidation and photooxidation in polypropylene.

TABLE IV
Performance of Metal-Organic Compounds as Stabilizers in Polypropylene

Stabilizer ^a	Stress-crack life, hr.	
	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
(<i>o</i> -Methoxybenzoylcyclopentadienyl)cyclopentadienyliron	5	510
(<i>o</i> -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.

The additives were compounded into the polypropylene by the same method given for the additives in Table I, except the polypropylene used here contained 0.3% of dilauryl 3,3'-thiodipropionate and 0.1% of 2,6-di-*tert*-butyl-*p*-cresol to minimize degradation during compounding and molding. Tensile bars were prepared as described previously and tested under stress, both in the 140°C. oven and in the modified Weather-Ometer.⁸ The stress-crack life of the samples was determined for both types of exposure and the values are shown in Table IV.

The metal complexes of 2,4-pentanedione exhibited a fairly wide range of stabilizing efficiencies. The nickel complex was of the greatest interest because of its efficiency as a stabilizer against photooxidation.⁹ Both nickel and copper complexes share the property of being good stabilizers against photooxidation while being antistabilizers toward thermal oxidation. On the other hand, the magnesium complex was mildly effective against both types of oxidation.

Derivatives of (benzoylcyclopentadienyl)cyclopentadienyliron have recently been publicized as stabilizers against photooxidation, particularly in outer space environments.¹⁰ The examples in Table IV behaved like the nickel and copper complexes of 2,4-pentanedione; they were effective stabilizers against photooxidation and catalyzed thermal oxidation. The *o*-hydroxy derivative was the most effective photostabilizer and the most active thermal prooxidant, as can be seen in Table IV. After several hundred hours' exposure in the Weather-Ometer, the exposed side of the stressed polypropylene tensile bars containing this additive remained in a smooth, shiny condition while the under side (away from the light) became cracked and crumbly. Failure occurred when these cracks propagated through from the underside to the exposed surface. A similar, though much less exaggerated, phenomenon was noted in polyethylene containing copper (II) stearate. Such samples, exposed either outdoors or in the Weather-Ometer, showed the development of a surface-cracking pattern on the undersides before any apparent damage occurred on the exposed surfaces.

Some metal-organic compounds can act effectively as stabilizers against both thermal oxidation and photooxidation in polypropylene, as shown by the last two examples in Table IV. One of these examples, nickel (II) dibutyldithiocarbamate, has long been known as an effective stabilizer against photooxidation of polyethylene.¹¹

The mechanisms of stabilization are, as yet, so incompletely understood that it is extremely hazardous to predict the performance of stabilizers in a new plastic medium on the basis of results obtained in a known medium. Such predictions have led to serious errors even though the new medium was chemically similar to the old. For example, the nickel complex of 2,4-pentanedione, as shown in Table IV, prolonged the Weather-Ometer stress-crack life of polypropylene by a factor of about six. The same concentration of this additive reduced the Weather-Ometer stress-crack life of polyethylene to about one half that of the unstabilized plastic. Simi-

lar results were obtained when these compositions were exposed outdoors at Kingsport, Tennessee.

It is likewise hazardous to rely on a single evaluating test to predict the overall performance of a stabilized composition. For example, the addition of the copper chelate of α,α' -(ethylenedinitrilo)di-*o*-cresol to polyethylene retarded the formation of carbonyl groups during photooxidation.¹² However, this same compound accelerated the onset of stress cracking during outdoor exposure. Table V shows the results obtained on this composition outdoors at Kingsport, Tennessee. Thus, it may be seen that the copper chelate of α,α' -(ethylenedinitrilo)-di-*o*-cresol might be considered a stabilizer by one interested in retention of electrical properties but an antistabilizer by one interested in retention of mechanical properties

TABLE V
Stabilization of Polyethylene With Copper Chelate of
 α,α' -(Ethylenedinitrilo)di-*o*-cresol

Amount of stabilizer	Increase in carbonyl content after 130 days, relative units	Stress-crack life, days
None	52	370
1%	47	112

Conclusion

Metal-organic compounds have been found to be effective as antioxidants, prooxidants, and ultraviolet stabilizers for polyolefins. Sometimes a given compound has activity in two of these categories. The mechanisms of stabilization are, as yet, so incompletely understood and the anomalies so frequent that it is extremely hazardous to transfer stabilization data from one polymer to another. It is even difficult to transfer stabilization data from one polyolefin to another, especially when a single evaluating test is the basis for the prediction of overall performance.

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Résumé

Au cours des dernières années, on a montré que certains composés organométalliques possédaient une efficacité particulière en tant que stabilisateurs dans la réaction de détérioration de polyoléfines et d'autres polymères sous l'action de l'oxygène. Ceci peut sembler surprenant étant donné l'effet catalytique bien connu de ce genre de composés lors de l'oxydation de substances organiques. En effet, on a observé qu'un composé organométallique donné peut agir comme stabilisateur pour un autre. De plus, dans un même système, le composé peut à la fois retarder un mode d'oxydation et en accélérer un autre. Par exemple, le chélate cuivrique de l' α, α' -(éthylènedinitrile)-di-*o*-crésol retarde la formation des groupements carbonyles et accélère la scission lors de la photooxydation du polyéthylène. Le but de cet article est de considérer un certain nombre d'exemples de ce genre tirés du domaine des stabilisateurs organométalliques. Une théorie générale de l'oxydation et de l'antioxydation permettent de rendre compte de telles anomalies curieuses.

Zusammenfassung

Während der letzten Jahre wurde berichtet, dass eine Anzahl organometallischer Verbindungen eine ungewöhnliche Wirksamkeit als Stabilisatoren gegen die oxydative Schädigung von Polyolefinen und anderen Polymeren besitzen. Das mag in Hinblick auf die wohlbekannt katalytische Wirksamkeit solcher Verbindungen bei der Oxydation organischer Stoffe überraschend erscheinen. Es wurde tatsächlich beobachtet, dass eine gegebene Metallverbindung in einem System als Stabilisator und in einem anderen als Antistabilisator wirken kann. Sogar in einem bestimmten System kann die Verbindung gleichzeitig einen Oxydationsvorgang verzögern und einen anderen beschleunigen. Zum Beispiel verzögerte das Kupferchelate von α, α' -(Äthylendinitril)-di-*o*-cresol die Bildung von Carbonylgruppen und beschleunigte die Spaltung während der Photooxydation von Polyäthylen. In der vorliegenden Mitteilung werden eine Anzahl von Beispielen dieser Art aus dem weiten Bereich der organometallischen Stabilisatoren betrachtet. Eine umfassende Theorie der Oxydation und Antioxydation sollte auch so merkwürdige Anomalien einschliessen.

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