

Antioxidants
Recent Developments

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ANTIOXIDANTS

Recent Developments

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NOYES DATA CORPORATION

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1979

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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents, issued since October 1974, that deal with antioxidants. This title contains new developments since our previous title *Antioxidants—Syntheses and Applications* published in 1975.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, commercially oriented review of recent developments in the manufacture of antioxidants.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data were employed to bring this durably bound book to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have by-passed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

15 Reasons Why the U.S. Patent Office Literature Is Important to You —

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.
2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."
3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.
4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.
5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.
6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.
7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.
8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.
9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.
10. Obtain licenses — many U.S. chemical patents have not been developed commercially.
11. Patents provide an excellent starting point for the next investigator.
12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.
13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.
14. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.
15. It is a creative source of ideas for those with imagination.

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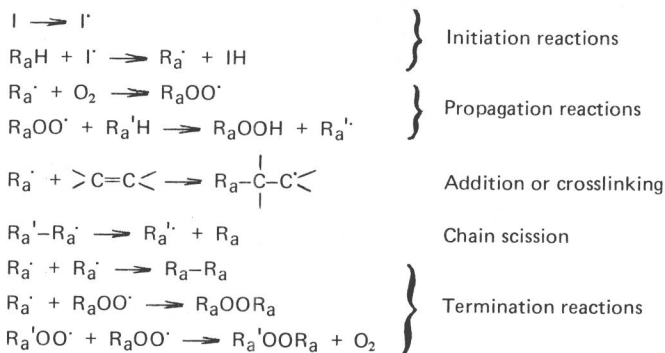
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INTRODUCTION

The function of an antioxidant is to prevent the oxidation of some organic material thus increasing the useful lifetime of that material. The process of oxidation is rather complex, but the following generalized scheme demonstrates the most important features of autooxidation processes.



I or IH is a species which forms the free radicals I^{\cdot} and R_aH is an organic substrate.

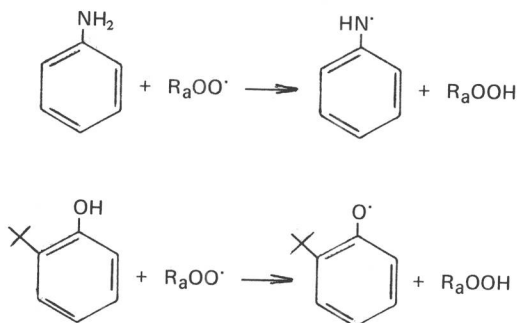
Any oxidation of organic materials requires an initiation process which generates free radicals from the substrate. These free radicals are able to react with atmospheric oxygen, a particularly facile reaction resulting from the diradical nature of the oxygen molecule, to give a peroxy radical. This peroxy radical is very reactive and will rapidly abstract a hydrogen atom from the surrounding medium or substrate to yield a new free radical and a hydroperoxide molecule. Since a new free radical is generated at each step, more oxygen is incorporated into the system as this chain reaction proceeds, and the reaction is terminated only when two free radicals combine to form a nonradical product.

During the course of the chain reaction chain scission can occur, usually with the introduction of an oxygen function into the molecule which often acts as a photosensitizer, absorbing light or ultraviolet radiation and generating further free

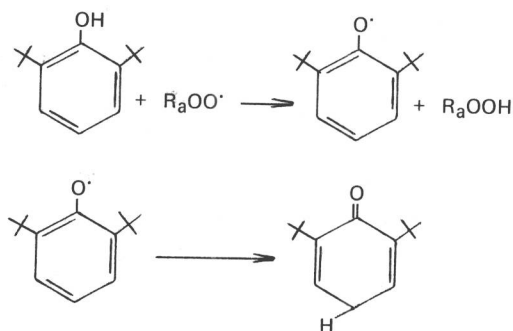
radicals to initiate further oxidation, introducing discoloration and, most important, breaking down the substrate molecules. In unsaturated systems, the free radicals can add to centers of unsaturation, generating a new free radical and joining two substrate molecules together. These are two of the destructive elements of oxidation, causing gross changes in the chemical and physical properties of the substrate.

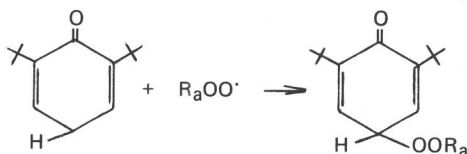
The hydroperoxide molecules generated in the propagation reaction are thermally unstable, and generally undergo heterolytic fission to yield two free radicals. These are able to initiate further chain reactions, and so the whole process may be said to be autocatalytic. In order to suppress oxidation, the addition of an antioxidant is required, and this may function in several ways, either interfering with the chain reaction mechanism or by suppressing initiation reactions.

The phenolic antioxidants and the aromatic amine antioxidants, for example, BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), methylene bisphenol and diphenylamines, act by interacting with free radicals present in the system, forming a nonradical substrate product and a phenoxy or phenimino radical by donation of a hydrogen atom from the antioxidant to the substrate radical:



If the resulting antioxidant radical is well stabilized, or sterically prevented from reacting further, then it will not act as an initiator of further reaction. It may, in fact, react with a second free radical in the system, thus interacting with two radical chain reactions.





The processes shown above do generate hydroperoxide molecules however, and so may only shorten the chain reaction, leaving behind a molecule capable of initiating a further chain of reactions.

A second type of antioxidant, of which dilauryl thiodipropionate is a typical example, functions in such a way as to remove hydroperoxide molecules from the system by a mechanism not involving free radicals.

The hydroperoxide molecule R_aOOH is bonded to the antioxidant via a hydrogen bond, and the steric arrangement is such that a bond migration occurs to yield an alcohol and an oxidized form of the thioether. The molecule containing the oxidized sulfur atom is capable of reacting with a further molecule of hydroperoxide. This mode of operation introduces hydroxyl groups into the substrate.

The phenomenon of synergism is also well-known. When two antioxidants, one a free radical inhibitor and the other a hydroperoxide decomposer, are used in combination, the overall effect is more than additive. Hence a mixture of butylated p-cresol (BHT) and dilauryl thiodipropionate (DLTDP) is commonly used to great effect in some polymer systems.

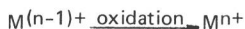
The reasons for this synergistic effect are quite obvious when looked at in the light of the scheme of oxidation previously set forth, since the removal of hydroperoxide molecules will grossly reduce the rate of chain initiation, and the radical inhibitor will stop the progress of any chain reactions, such as those initiated by photosensitization or by the presence of traces of metal oxidation catalysts. Any hydroperoxide molecules generated will be eliminated by the hydroperoxide decomposing antioxidant. This synergistic effect is illustrated by the following data.

Compound	Induction Period in Liquid Paraffin at 150°C (hr)
2,2'-Methylenebis(6-tert-butyl-4-methylphenol)	12.7
Di-n-decyl sulfide	12.2
Combination of above at same concentrations	54.7

A third type of stabilizer which can prevent oxidation occurring is the metal deactivating antioxidant. Initiation of oxidation can be brought about by the electron exchange reaction between the substrate and a metal ion of variable valence, for example:



Here the metal is reduced and a free radical is produced. The metal ion may subsequently be reoxidized by oxygen from the atmosphere or by other mechanisms to regenerate the oxidation catalyst:



This process of initiation is well known and is used purposely to initiate oxidation in processes such as the drying of paint films, where materials such as cobalt naphthenate are employed. The requirements of such oxidation catalysts is that the valency state is stabilized by the ligands both before and after oxidation. The usual method of deactivating adventitious metal catalysts is by complexing them in a system where only one valency state is stable or by removing them as inorganic metal salts.

An antioxidant should be nonvolatile. If a volatile antioxidant is used, it is likely that some of it will be lost from the system during processing or during use leaving behind a nonstabilized product. The volatility of an antioxidant is related to its molecular weight, and hence in this respect at least, compounds of high molecular weight are advantageous. Over the years, the development of antioxidants with increasing molecular weight is readily seen in the literature, progressing from simple phenols such as BHT, with a relatively high volatility, through the bisphenols to molecules where 3, 4 or even 5 molecules of a 2,6-disubstituted phenol are incorporated into one molecule.

Another important factor in the choice of an antioxidant is the degree of compatibility between the antioxidant and the substrate. If the two are incompatible, compounding becomes difficult and the antioxidant will tend to form aggregates in the system, leaving large volumes of unstabilized material. Since the centers of antioxidant activity are, in general, polar groups, there is a certain incompatibility between substrate and antioxidant. This can be overcome by incorporating hydrophobic groups into the molecule. This, however, increases the molecular weight of the compound, and hence lowers the antioxidant activity of the compound on a weight for weight basis.

The conflicting effects of simultaneously increasing the molecular weight of the antioxidant and its compatibility with the substrate continue to be the subject of considerable research effort.

This book, based on the recent patent literature of the United States represents over 250 processes and literally thousands of antioxidative compounds, mixtures and formulations. In general, because of the mechanistically common oxidative degradation pattern of most organic substances, these antioxidative compositions are widely applicable to a variety of products used in modern society. Additionally, where related, antiozonants and ultraviolet stabilizers have been included.

This book, largely applications oriented, thus provides antioxidant compositions and end-use formulations for polyolefins, PVC, other common plastics, elastomers, lubricants and food products, while fully recognizing the multisystem adaptability of most antioxidant compounds.

POLYOLEFIN RESINS

Polyolefins are subject in many applications to degradation caused by the deleterious effects of heat and light. Many stabilizers have been used to protect such polymers from degradation but they have not been completely satisfactory in providing protection from both heat and light degradation, and often introduce color problems. Aromatic sulfur compounds have been used as heat stabilizers for rubber and polyolefins including (5-methyl-3-*t*-butyl-2-hydroxyphenyl) monosulfide. Symmetrical polyhydroxy compounds such as 4,4'-thiobis(resorcinol) and the like have been used in bleaching and stabilizing wood rosin. However, such materials have not been completely satisfactory in providing both heat and light resistance to polymers exposed to heat and light, particularly the polyolefins.

Polypropylene is a tough, hard, relatively flexible, high-melting polymeric material, and thus has a number of important applications, such as, for example, as electrical insulation for copper wires and cables. However, in several respects the stability of polypropylene leaves much to be desired. The polymer shows a tendency to decrease rapidly in melt viscosity and then to become brittle when kept at elevated temperatures for the time required in milling, calendering, extrusion, injection molding, and fiber-forming equipment. This deterioration is particularly serious when the polymers are worked in a molten state in the presence of oxygen, for example, air. It is known in the art that degradation in one or more physical properties of polypropylene due to heat can be inhibited by the incorporation of a number of well-known thermal antioxidants, including hindered phenols, secondary aromatic amines, organic phosphites, and thioldi-propionic acid esters.

PHENOLIC COMPOUNDS

Complexed Hindered Phenol

F. Scardiglia and K.D. Kiss; U.S. Patent 4,049,751; September 20, 1977; assigned to Dart Industries Inc. describe a primary antioxidant composition which com-

prises a complex of hindered phenolic antioxidant and a high molecular weight nitrogeous complexing agent derived from compounds selected from the group consisting of N-vinyl pyrrolidone and N-dialkyl substituted amino alkyl esters of α,β -unsaturated carboxylic acids.

The polyolefin base resins to be stabilized with the antioxidant complex comprise solid, substantially crystalline polyolefins including homopolymers and copolymers of α -olefins having 2 to 8 carbons and blends thereof. Among the preferred polyolefins are the polypropylene based resins containing at least 60% by weight, preferably at least 75% polymerized propylene groups, e.g., propylene homopolymer and the ethylene-propylene polymer resins, such as random or block copolymers of ethylene and propylene, blends of homopolymers of propylene and ethylene, and various combinations thereof, wherein the ethylene in either homo- or copolymerized state accounts for from about 2 to 25% by weight of the total resin and more preferably from about 3 to 15%.

Example 1: A graft copolymer of N-vinyl-2-pyrrolidone grafts on polypropylene was prepared by charging 100 parts by weight polypropylene powder (average particle size in the range of 0.01 to 4 mm), 5 parts N-vinyl-2 pyrrolidone (NVP) and 1 part t-butyl peracetate (75% solution in benzene) to a reactor equipped with a stirrer. The ingredients were well mixed and had an overall dry appearance. The system was purged with argon and the reactor was heated to 125° to 130°C under autogeneous pressure. The mixture was maintained at this temperature for 4 hours, followed by cooling and devolatilization with vacuum and direct recovery of the reaction product in particle form. Similar graft copolymers were prepared using essentially the above procedure except for variation in the NVP content (respectively 0.25; 0.75 and 1.5 parts per 100 parts polypropylene).

Example 2: A graft copolymer of 5 parts by weight N,N-dimethylaminoethyl methacrylate (DMAEMA) per 100 parts polypropylene powder (particle size 0.01 to 4 mm) was prepared following the general procedure of Example 1, except that DMAEMA was used instead of NVP and the reaction was carried out for 5 hours instead of 4 hours.

Examples 3 through 13: Ungrafted polypropylene and the grafted polypropylenes from Examples 1 and 2 were blended with the amounts of primary and secondary stabilizers indicated in the table below until homogeneous compositions were obtained. The parts given are parts per 100 parts polypropylene.

Each of the blended samples was then compression molded into 6" x 6" x 10 mil plaques at 400°F and 25,000 psig for 60 seconds. The plaques were rapidly cooled at high pressure and cut into 1½" x 1½" x 10 mil strips. One set of strips was submerged in USP Grade petrolatum at 86±1°C for 18 hours. The strips were removed from the petrolatum, wiped clean and tested using differential scanning calorimetry (DSC). This analysis provides an extremely effective method for obtaining accelerated aging data which can be extrapolated to periods of decades at ambient temperatures.

The controls and examples were all tested by the following DSC procedure: A small sample of the 10 mil film strip prepared in the compression mold having a diameter of approximately 0.25 is placed on a copper test pan in a Perkin-Elmer differential scanning calorimeter (DSC). The pan is then covered and heated from room temperature at a linear programmed rate of 10°C/minute in