ANTIOXIDANTS
Syntheses and Applications

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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents since 1972 relating to antioxidants. Where it was necessary to round out the complete technological picture, some earlier, but very relevant patents were included.

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, technically oriented review of antioxidants and their synergists.

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 are employed to bring our new durably bound books 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 bypassed 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.

FOOD ADDITIVES TO EXTEND SHELF LIFE 1974

by Nicholas D. Pintauro

Food Technology Review No. 17

Aside from freezing, canning and sophisticated methods of packaging, food is preserved by dehydration, salting, sugaring, smoking, curing, and certain types of fermentation.

A newer effective approach toward prevention of spoilage is by the use of chemical additives other than sugar, salt, vinegar, and spices.

Food additives, as defined by the National Academy of Sciences are those relatively nontoxic chemicals that may be incorporated into foodstuffs during the growing, processing, or storing periods. Every chemical added must serve one or more of these general purposes: Improve or maintain nutritional value, enhance quality, increase consumer acceptability, and facilitate preparation. In modern applications food additives are combined with established, classical methods of food preservation to maximize stability for extended shelf life. There is a great demand for additives to prevent or retard food deterioration. These additives include antioxidants, antibacterial agents, mold inhibitors, color stabilizers, anticaking agents, antibrowning agents, cloud stabilizers, metal scavengers, enzyme inhibitors.

This book describes over 140 processes involving the newest technology available in the U.S. patent literature using food additives. A partial and condensed table of contents follows here. Chapter headings are given, followed by examples of important subtitles.

ISBN 0-8155-0548-0

402 pages

FUEL ADDITIVES 1974

by M. William Ranney

Chemical Technology Review No. 26

The search for improved fuel additives has taken on new and significant dimensions with the pending world-wide fuel shortage. The mid-seventies are expected to be a time of increasingly short fuel supplies which could drastically curtail our production capability, our personal travel patterns, and in the long run, our gross national product and our very way of life, while at the same time reversing the ecological progress made to date.

Successful research for more effective additives, which really increase mileage or BTU output of the fuels in question, will provide many new business opportunities in the next few years. Fuel additives manufacture and sales can be expected to show well above normal growth over the next decade.

This book describes almost 200 processes, including many fuel additive formulations which appeared in the U.S. patent literature during just the past three years. A partial and condensed table of contents follows. Numbers in ( ) indicate the number of processes per topic. Chapter headings are given, followed by examples of important subtitles.

ISBN 0-8155-0525-6

273 pages

FIRE RESISTANT AND FLAME RETARDANT POLYMERS 1974

by Maurice William Ranney

Chemical Technology Review No. 35

The U.S. market for these materials is a hundred million dollar annual business and is expected to double within the next three years. This includes reactive intermediates and non-reactive additives which impart fire retardance to plastics, foams, textile fibers and paints.

Such flame retardant additives and reactive intermediates are now available for most polymer systems. While many proven formulations rely on additives containing halogen, such as chlorinated wax and tris-(dibromopropyl) phosphate, commonly in combination with antimony oxide, much recent technology has been directed toward building flame retardance into the polymer nucleus, using reactive intermediates.

Self-extinguishing polyesters, employing halogenated dicarboxylic acids or anhydrides, and polyurethanes based on phosphorus-containing polyols are now finding increased use by the industry.

This book provides an in-depth look at over 250 processes. Directions are adequate enough to make manufacturing decisions by an industry which is faced with great responsibilities and opportunities as increasing public and governmental attention is focused on the need for improved flame retardant products.

A partial and condensed table of contents follows. Numbers in ( ) indicate the number of processes per topic.

ISBN 0-8155-0541-8

395 pages.

CONTENTS AND SUBJECT INDEX

INTRODUCTION

Antioxidants can be defined as substances capable of slowing the rate of oxidation in an autoxidizable material. Commercially, antioxidants are used in plastics, elastomers, petroleum products, synthetic lubricants, food products, soaps and cosmetics. In plastics and elastomers they are particularly needed to overcome the exposure to heat and oxygen during processing and in use. The petroleum and synthetic lubricants are also required to withstand extremely high temperatures in today's automotive and jet engines without excessive breakdown.

Without the antioxidants our foods would become rancid, plastics become brittle and crack, tire sidewalls craze and eventually fail, and fuels and lubricants will corrode equipment and require shutdown for repair or replacement. Good antioxidants are therefore a valuable commercial commodity, particularly for the polymer (including elastomers) and petroleum industries.

In selecting patents to be covered in this review, the term antioxidant was applied in a strict sense of the term. Materials used to improve stabilization such as heat stabilizers for PVC, ultraviolet stabilizers for polyolefins, acid acceptors, dispersants and the like for lubricants were not included. However, antiozonants were considered a special form of antioxidants and were included in the review. Multicomponent stabilizing systems containing antioxidants or antiozonants were also included.

Most of the 247 patents covered in this review were issued since 1972. The old time standbys, the phenol and amine antioxidants, are still being synthesized. However, many of the new compounds produced as antioxidants combine a hindered phenol group with another group containing sulfides, triazine, phosphates, phosphites, etc. which give active materials hopefully having the advantage of two or more stabilizing moieties.

TEST METHODS

Various test methods have been used repeatedly throughout the book. To avoid unnecessary repetition, the procedures are given here for reference purposes.

Oven Aging Test

Unstabilized polymer powder is thoroughly blended with an antioxidant. The blended material is then milled on a two roller mill at 182°C for 10 minutes after which time the stabilized polymer is sheeted from the mill and allowed to cool.

The milled polymer sheet is then cut into small pieces and pressed for 7 minutes on a hydraulic press at 218°C and 2,000 psi pressure. The resultant sheet of 25 mil thickness is cut into small plaques and tested for resistance to accelerated aging in a forced draft oven at 150°C.

Fadeometer Test

The 25 mil plaques prepared as described in the Oven Aging Test are placed on a white card stock background and exposed in a Fadeometer. The specimens are tested for embrittlement at 20 hour intervals by bending them 180°. The result of this test is recorded as the number of hours the specimen stayed in the Fadeometer until a clean break is obtained.

Weatherometer Test

Solid polymer is milled in a two roll heated mill and the additive is incorporated in the sample during the milling. The samples are pressed into sheets of about 17 mil thickness and cut into plaques of about 1⅞" x 1½". The plaques are inserted into plastic holders, affixed onto a rotating drum and exposed to carbon arc rays at about 52°C in a Weatherometer. The samples are examined periodically by infrared analysis to determine the carbonyl band at 1,715 cm^{-1} which is reported as the carbonyl number. The higher intensity of the carbonyl band indicates a higher carbonyl concentration (expressed as carbonyl number) and accordingly increased oxidation.

Falex Machine Test

This procedure is described in detail in *Lubricant Testing* by E.G. Ellis published by Scientific Publication Limited (Great Britain), 1953, pages 150-154. It is also described on pages 21-1 and 27-2 of the *Handbook of Lubrication Engineering,* O'Conner, editor, McGraw Hill 1968.

Briefly, the Falex machine consists of a rotating pin which runs between two V-shaped bearings which are spring loaded against the pin and provided with means for varying the load. The oil to be tested is poured into a metal trough in which the pin and bearings are partly submerged. The machine is operated for 5 minutes each at 250 and 500 pound loads and then 45 minutes at 750 pound load. The data collected include the temperature of the oil at each of the loads, as well as the wear which is determined by a ratchet wheel arrangement in which the teeth are advanced in order to maintain the desired load. Each tooth is equivalent to approximately 0.000022 inch.

In another series of tests the machine is operated for 5 minutes at each load from 250 lb to seizure at 250 lb increments. The maximum load, the time in minutes at this load to seizure are reported, as well as the temperature of the oil. In this case the higher temperature is preferred because it means that the oil is operating satisfactorily at a higher temperature.

PHENOLIC ANTIOXIDANTS

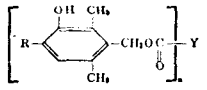
Phenolic compounds comprise one of the oldest and most frequently used category of antioxidants. Foremost among the phenols are the so called hindered phenols in which the aromatic ring contains alkyl groups, preferably branched groups such as tert-butyl. The hindered phenol moiety appears in many of the antioxidants produced in recent years, frequently combined with other active antioxidant groups.

HINDERED HYDROXYBENZYL ALCOHOL DERIVATIVES

Esters of 3-Hydroxybenzyl Alcohols

Antioxidants useful in many organic materials have been prepared by *J. Song and H. Richmond; U.S. Patent 3,795,700; March 5, 1974; assigned to American Cyanamid Co.* from phenol alcohols having three alkyl groups.

More particularly, these antioxidants are compounds of the formula:



where R is branched chain alkyl group containing three to twelve carbons; Y is the residue of the carboxylic acid $Y(COOH)_n$, provided that when Y is alkyl and n is one, Y contains more than ten carbons; and n is one to four.

Illustrative of the branched chain alkyl groups represented by R ortho to the phenolic hydroxy group and para to the ester group are isopropyl, tert-butyl, sec-butyl, tert-amyl, sec-heptyl, sec-octyl, tert-octyl, tert-nonyl (1,1-dimethylheptyl), α,α-dimethylbenzyl, methylcyclopentyl, methylcyclohexyl, and the like.

Illustrative of the carboxylic acids $Y(COOH)_n$ of which the moiety Y forms part of these compounds are monocarboxylic acids such as stearic, myristic, palmitic, benzoic, naphthoic, salicylic, phenylglycolic, pyridinecarboxylic, mesitoic, oleic, and the like; dicarboxylic acids such as 3,3'-thiodipropionic, phthalic, hexahydrophthalic, terephthalic, adipic, p-phenylenediacetic, oxalic, malonic, succinic, pimelic, azelaic, sebacic, homophthalic, maleic, fumaric,