

FOOD TECHNOLOGY REVIEW No. 17

Food Additives to Extend Shelf Life



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FOOD ADDITIVES TO EXTEND SHELF LIFE

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Park Ridge, New Jersey

London, England

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FOREWORD

The detailed, descriptive information found in this book is based on U.S. patents relating to chemical additives which can be used in foods to prolong their shelf life. 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 how to prolong the shelf life of foods by means of chemical additives.

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."

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.

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

100

15 Reasons Why the U.S. Patent Office Literature is important to You -

- 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.
- The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure"
- 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.
- Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.
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- 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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INTRODUCTION

Primitive man was restricted to the food supply immediately at hand. This supply was determined in both quality and quanity by the soil and climate. When there was sufficient quantity, man devised methods to protect and extend his food supply beyond the immediate future and sometimes to the next season by sun-drying, salting, fermenting, smoking and other simple methods. Modern food manufacturers use canning, freezing, refrigeration, dehydration, and modern packaging as methods of preservation. Another effective modern approach for protection against spoilage is the use of additives.

Food additives, as defined by the National Academy of Sciences, are those chemicals that may be incorporated in foodstuffs, either directly or indirectly, during growing, storage or processing of foods. Every chemical should serve one or more of these general purposes: improve or maintain nutritional value, enhance quality, enhance consumer acceptability, improve keeping quality, and facilitate preparation. In modern applications, food additives are combined with classical methods of food preservation to maximize stability for extended shelf life.

One of the most important factors producing food deterioration is oxidation. Food oxidation occurs when the oxygen present unites with other chemical elements or groups of elements in foods to form oxides which cause the breakdown of fatty or other carbohydrate food components resulting in the ultimate deterioration of protein matter. The reactions arising out of and accompanying oxidation are believed to cause various chemical and biological changes resulting in such undesired results as rancidification of fats, molding of carbehydrates and putrefaction of proteins. Basically, the undesirable effects of food oxidation appear to stem primarily from microorganism activity and chemical changes and/or reactions.

All organic foods also contain microscopic forms of parasitic plant and vegetable life called microorganisms which live on larger forms of life. Among the most common microorganisms in food, useful to man and animal, are bacterial molds and yeasts. Not all such microorganisms, however, are necessarily harmful or undesirable. For example, lactic acid bacteria are usefully employed in making sauerkraut from fresh cabbage and silage from fresh grass. In most foods, however, the excessive growth of yeast, bacteria or molds indicates and accompanies spoilage.

In addition to microorganisms, raw organic foods contain substances called enzymes which appear to act somewhat as organic catalysis. A common example of such activity is demonstrated in the fruit ripening process. Even after the fruit is picked, enzyme activity

continues, and if not halted, eventually will cause the fruit to spoil and rot. Generally speaking, enzymes act upon foods in two ways: either to add to or reduce water content or take up oxygen. There are three generally recognized types of food enzyme activities: lipolytic, amylolytic and proteolytic, and each type produces marked effects which can contribute either to the spoilage or the preservation of foods.

For instance, lipoxidase, which is a member of the lipolytic enzyme family, acts on fats and may cause butter, for example, to turn rancid. Cellulase and diastase, contrastingly assist in the preservation of foods by converting cellulose and starches into sugars, alcohol and esters, the latter giving the characteristic flavors to foods. Cellulase is especially effective in hydrolyzing cellulose, while diastase, being high in alpha-amylase with some beta-amylase, is particularly active on starches. The proteolytic enzyme family includes, by way of example, papain, ficin, bromelin and others which generally act to hydrolyze and reduce proteins.

It is generally acknowledged that the processes and evolutions involved in food spoilage and deterioration are not fully understood, but it is known that they are greatly accelerated by the presence of air, moisture and heat, particularly in excessive amounts. Since these factors are naturally present, it is extremely difficult to preserve and store foods without taking abnormal precautions to avoid these factors. For example, the surface exposure of foods to air greatly accelerates rancidification of fatty components, which action weakens the natural antioxidants present in foods and thereby helps to bring about complex adverse effects on enzyme splitting systems which are interlocked in the protein, carbohydrate and fatty food constituents. In this way, food becomes susceptible to destructive attack by bacteria, molds and yeasts.

In the tremendous expansion of the food industry in the past twenty years there have been great strides to formulate, process and package foods to provide greater stability and longer shelf life. Consequently, there has been 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, etc.

Food additives classified as preservatives totaled 50 million pounds in the United States in 1965. It is expected that this volume will reach 75 million pounds by 1975 for a value of \$50 million at the chemical manufacturers' level. Processes for use of additives to extend shelf life of foods, as given in this volume, are organized according to food category or food group. It is believed that this approach will be better for the understanding of the reader than if the additives are discussed according to their function in several food groups. In addition, there is an index of additives at the end of the book.

The three Appendices include general information on food additives as published by the National Academy of Sciences, selected abstracts from the Federal Food, Drug, and Cosmetic Act, and several recent pronouncements on policy in the Federal Register by the Food and Drug Administration.

ANTIOXIDANTS FOR FATS AND OILS

BHA AND METHYL ANTHRANILATE

Rancidity is one of the major contributors to deterioration of fatty materials and is greatly promoted by the influence of air, heat, heavy metal ions, moisture and similar factors. It is well known that antioxidant materials may be effectively added to fats and oils to preserve them, principally by opposing oxidation and inhibiting related reactions promoted by oxygen and/or peroxides which are thought to be largely responsible for rancidification. Among the more common antioxidants commercially used for this purpose are such materials as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), nordihydroquaiaretic acid, ethoxyguin, propyl gallate, ascorbic acid and tocopherol.

Certain of these antioxidants appear to be more efficient in combination with one another and therefore various blends and compositions of antioxidant materials are offered commercially as fat preservatives according to the manufacturers' specifications. Rarely, however, do such compositions contain more than approximately 60% active ingredients.

A typical commercial formulation for an antioxidant fat preservative, for instance, consists of 20% BHT, 20% BHA, 10% propyl gallate, 10% citric acid and 40% carrier. While citric acid is not an antioxidant by itself, it appears to increase the activity of the commonly used antioxidants, promoting their general effectiveness and capabilities. Citric acid therefore, is referred to commonly as a synergist because of its apparent ability to increase the activity of the antioxidants over and above their normal capabilities.

While such known antioxidant compositions and formulations have proven generally successful in their application as preservatives for fats, oils and fatty substances, nevertheless they are limited in their application and effectiveness. Among such limitations is their limited capability of preserving fatty substances over prolonged periods. Additionally, most such commercially available antioxidant compositions readily break down and are ineffective at temperatures substantially in excess of 180°F. This means that these known preservative #laterials have little or no active ability to restrict and control unfavorable oxidative reactions which take place during normal cooking and rendering processes when reducing raw fatty substances to commercial grade products.

As a result, practice dictates the use of these materials by adding them to the fats after the latter have been rendered and cooled to temperatures below 180°F. This means that normal autooxidative reactions which are accelerated by the extremes of atmospheric oxygen, moisture and heat, present in the rendering processes, remain unchecked during the

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rendering stages so that the burning of carbonaceous materials and oxidative rancidity take place freely in the rendering stages. This leads to lower quality of the produced fats and cracklings, particularly as to color and free fatty acid values which greatly affect their commercial value.

In the area of edible fats, particularly those used in animal foods, for example, such known synthetic antioxidant preservatives are further subject to certain limitations and restrictions of use due to their known toxic effects at higher percentages. Consequently, tallows and greases which are preserved by known antioxidant preservatives, applied within their permissible nontoxic limits, cannot, as a rule, be sufficiently stabilized against rancidity thereby, to prevent their eventual contamination and loss of quality and palatability.

With respect to stabilization periods, one of the more accepted methods for determining the degree of stabilization of fats treated with antioxidants is based on the number of hours' protection afforded to the fat. This is determined by the Accelerated Oxygen Method of testing stability and is commonly referred to as Hours AOM Protection. Recognized authorities on fat stabilization, more particularly The American Meat Institute, recommend 20 hours AOM Protection as the minimum standard requirements for preservation of fats. This period is said to be equivalent to substantially 6 months' protection against rancidity under refrigerated storage conditions.

An effective combination of antioxidant materials is described by *T.B. Tribble and E.L. Rondenet; U.S. Patent 3,318,819; May 9, 1967; assigned to Flavor Corporation of America.* The combination consists of known antioxidant materials such as BHT and BHA, and ortho-aminobenzoic acid (anthranilic acid) or its esters, such as methyl anthranilate and ethyl anthranilate.

Free fatty acid content of fats is a determinative indication of the rate of oxidative potential. In general, free fatty acid (FFA) results from the breakdown of fat with the dissipation of glycerine, leaving fatty acid. The FFA number of fat analysis refers to the percentage of free fatty acid present, and generally speaking, fats having a low FFA number are preferred and considered to have a greater commercial value and quality than fats with higher FFA numbers. It has been found that these fat preservatives are very effective in lowering the FFA or free fatty acid content of the treated product.

In addition to the free fatty acid content, the color rating of fat is also commercially important. Color rating is referred to as the FAC color number in fat analysis; the same being based on a color reading matched against samples of fat having standardized colors as recommended by the Fat Analysis Committee of the American Oil Chemists' Society. Generally speaking, the FAC color number usually assays substantially one or two times the FFA acid number and since this ratio appears to be fairly consistent, the two numbers are deemed to have an interrelationship. This relationship is demonstrated by the lowering of the FFA or fatty acid number of fat being accompanied by a lowering of the FAC color number as well.

In theoretical consideration, the higher the FFA number of fat, the greater amount of antioxidant required to stabilize the same against oxidative rancidity. Fats having high acid numbers are usually classified as inedible and unfit for human consumption, although they are acceptable for use in animal foods. Since this preservative demonstrates a definite ability to lower the free fatty acid content of fats treated therewith, it likewise has the ability to lower the FAC color number, thereby resulting in finished greases and tallows having low FAC color ratings.

Still another characterizing feature of these preservatives resides in the apparent continuing operative activity of the antioxidant material in the treated fats after rendering. This continuing antioxidant activity brings about a progressive decline in both the acid and color number values of fats even after the same are placed in storage after rendering. This feature therefore causes fats treated with these antioxidant preservatives to show progressive improvement in FFA acid number and FAC color number while in storage, resulting in

improvement of their commercial value. Some of the results produced by the antioxidant treatments are illustrated in the following Table 1

TABLE 1: NORMA-HOFFMAN STABILITY

| | Sample Treated at Temperatures Below 180°F | Time to 5-lb Pressure Drop, hr* |
|----|--|---------------------------------|
| 1 | Untreated choice-grade tallow | 2.0 |
| 2 | Tallow plus 0.05% anthranilic acid | 2.0 |
| 3 | Tallow plus 0.05% methyl anthranilate | 3.0 |
| 4 | Tallow plus 0.05% citric acid | 2.5 |
| 5 | Tallow plus 0.025% citric acid plus 0.025% anthranilic acid | 3.0 |
| 6 | Tallow plus 0.05% BHA | 3.0 |
| 7 | Tallow plus 0.05% BHA plus 0.025% anthranilic acid | 3.5 |
| 8 | Tallow plus 0.05% BHT | 5.0 |
| 9 | Tallow plus 0.05% BHT plus 0.025% anthranilic acid | 5.5 |
| 10 | Tallow plus 0.009875% BHT plus 0.0046875% methyl anthranilate | 3.75 |
| 11 | Tallow plus 0.046875% plus 0.00234375% methyl anthranilate | 2.5 |

^{*}Norma-Hoffman Bomb Test

The information of Table 1 demonstrates the stability of choice-grade tallow, both in an untreated state, that is, without synthetic preservatives added and the comparative effect of certain recognized antioxidant preservative materials along with the improved results obtained by the special antioxidants. The indicated results were obtained by treating the rendered tallow at temperatures below 180°F according to the Norma-Hoffman bomb test as specified by the American Oil; Chemists' Society. In this respect, the Norma-Hoffman test determines the time required for the fat sample to oxidize under certain accelerated conditions. This is brought about by placing the sample in an enclosed chamber into which excessive oxygen is introduced until an atmosphere having a constant pressure, substantially 15 psi is obtained.

Thereafter heat is applied to the chamber or bomb and the time required for the bomb's atmospheric pressure to drop 5 psi is then measured as determining the time required for the sample to oxidize. Viewed in another manner, this time is indicative of the oxygen interception ability of the stabilizing additive. Thus, the hour figures set out in Table 1 indicate the time required for oxidation of the test sample under the accelerated test conditions, with the higher time values indicating a greater resistance to oxidation.

As noted, Sample 1, the untreated choice-grade tallow, had a bomb test time of 2 hours. It will be noted that the addition of 0.05% methyl anthranilate to the tallow (Sample 3) resulted in a bomb test time of 3 hours, showing a marked increase in the treated tallow's ability to resist oxidation. The addition of citric acid to the tallow, as demonstrated by Sample 4, served to increase the bomb test time for the tallow by \$10 hours, while in Sample 5, the addition of one-half the amount of citric acid employed in Sample 4 plus an equal amount of anthranilic acid resulted in a bomb test time greater than that obtained by Sample 4, treated with the citric acid.

The results obtained from Samples 6 and 7 in Table 1 illustrate the ability of anthranilic acid to increase the antioxidant effect of BHA, with similar relationship as to BHT being demonstrated by the observed results of Samples 8 and 9. The results of utilizing comparatively minor nontoxic amounts of BHT and methyl anthranilate in combination are found in the results obtained from Samples 10 and 11 which compare favorably with results obtained from Sample 7, for example, containing toxic percentages of the antioxidant. In this respect, the recognized total toxic limit for the antioxidant additives, such as BHT or BHA, is 0.02% for edible fats prepared for human consumption and 0.05% for

fats used in animal feeds. The most effective results obtained appear in Sample 9 wherein BHT and anthranilic acid are combined in a ratio of substantially 2:1 and a total additive percentage of 0.075%, giving an extended bomb test time of 5.5 hours, compared to the untreated tallow bomb test time of the 2 hours, as seen in Sample 1. Generally speaking, it is apparent that the utilization of methyl anthranilate or anthranilic acid, particularly in combination with known antioxidents such as BHA or BHT, effectively extends the stability of the tallow. The following Table 2 further serves to illustrate some of the results, based on AOM stability findings.

TABLE 2: HOURS AOM STABILITY

| | Sample Treated at Temperatures Below 180°F | AOM Stability, hr |
|---|---|-------------------|
| 1 | Untreated choice-grade tallow | . 5 |
| 2 | Tallow plus 0.05% citric acid | 5.5 |
| 3 | Tallow plus 0.05% anthranilic acid | 7.0 |
| 4 | Tallow plus 0.05% methyl anthranilate | 5.5 |
| 5 | Tallow plus 0.01875% BHT plus 0.009875% methyl anthranilate (0.028625% total) | 81 |
| 6 | Tallow plus 0.01875% BHT plus 0.009875% methyl anthranilate plus 0.05% citric acid (0.07625% total) | 113 |
| 7 | Tallow plus 0.0375% BHT plus 0.01875% methyl anthranilate (0.058% total) | 113 |
| 8 | Tallow plus 0.05% BHT plus 0.025% anthranilic acid (0.975% total) | 121 |

The untreated choice-grade tallow, Sample 1, demonstrates an AOM stability of 5 hours. By adding 0.05% citric acid to the tallow (Sample 2) at temperatures below 180°F, the AOM stability was increased by ‰ hour. By comparison, in Sample 3, the addition of 0.05% anthranilic acid to the tallow increased its AOM stability to 7 hours, while the substitution of the same percentage of methyl anthranilate in Sample 4 produced results equivalent to that produced by the citric acid additive utilized in Sample 2.

Sample 5 shows the effect of using nontoxic percentages of the antioxidant. It also will be noted that the hours AOM obtained from Samples 6 and 7 are identical, although the total percentage of the additive ingredients employed in Sample 7 is substantially less than that employed in Sample 6. In this respect, the percentages of BHT and methyl anthranisate in Sample 7 are twice the percentages of those ingredients in Sample 6, but the citric acid has been eliminated from Sample 7. In each instance, however, the BHT and methyl anthranisate been a ratio of substantially 2:1.

Sample 8 of Table 2 shows the greatest number of hours AOM stability obtained utilizing BHT and anthranilic acid in a ratio of 2:1 and a total ingredient percentage just slightly less than that utilized in Sample 6, where BHT and citric acid combination was used. The following Table 3 serves to illustrate some of the results produced in achieving stability in acid and color.

TABLE 3: COMPARATIVE ACID AND COLOR VALUES

| | Sample | FAC Color No. | FFA Acid No. |
|---|--|---------------|--------------|
| 1 | Choice-grade tallow (untreated) | 9 | 1.9 |
| 2 | Tallow plus 0.0125% BHT plus 0.00625% citric acid treated at 225°F | 9 | 1.9 |
| 3 | Tallow plus 0.0125% BHT plus 0.00625% methyl anthrapilate treated at 225°F | Less 3 | 1.2 |

As shown in Table 3, the untreated choice-grade tallow of Sample 1 showed an FAC color number of 9 and an FFA acid number of 1.9. After treating the tallow of Sample 1 with

a combination BHT-citric acid preservative, as in Sample 2, there were no observed changes in either FAC color number or FFA acid number over the Sample 1 findings. By way of contrast, the tallow of Sample 3, treated with BHT and methyl anthranilate, showed a marked depression in color number to less 3 scale value with a corresponding lowering of the free fatty acid number to 1.2. It will further be observed that both Samples 2 and 3 were treated at 225°F, substantiating the ability of the methyl anthranilate to promote antioxidant activity, particularly at elevated temperatures, while lowering the acid and color numbers of the resulting rendered product.

BUTYLATED HYDROXYTOLUENE (BHT)

The antioxidant of L.A. Hall; U.S. Patent 2,981,628; April 25, 1961; assigned to The Griffith Laboratories, Inc. is known as 2,6-di-tertiary-butyl-4-methylphenol, and known also as butylated hydroxy toluene. This material can be used in very small proportions, gives long shelf-life to fat and oil products, and carry-through to baked products such as crackers and cookies. It is also useful with fats or oils of either vegetable or animal origin. The product is not only antioxidant, itself, but forms synergistic mixtures with other well-known antioxidants. Examples of such synergistic antioxidant compositions are as follows. All the ingredients are shown in pounds.

| | · · · · · · · · · · · Examples · · · · · · · · · · · · · · · · · · · | | | | | | |
|--------------------------|--|-------|-------|-------|---------------|-------|-------|
| • | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Di-tert-butyl-p-cresol | 15.00 | 26.40 | 20.00 | 14.00 | 33.00 | 20.00 | 10.00 |
| Propyl galiate | 3.34 | 6.70 | | | | | |
| Citric acid | 3.74 | •• | 4.00 | - | 3.35 | | |
| Citric acid (anhydrous) | - | 3.35 | - | | | 4.00 | 4.00 |
| Lecithin | 22.68 | 20.10 | •• | | 20 .10 | | |
| Corn oil | 55.24 | 43.45 | | •• | 43.55 | 60.00 | 60.00 |
| Butylated hydroxyanisole | - | • | 6.00 | 14.00 | | | 10.00 |
| Propylene glycol | | | 70.00 | | | | |
| Lard oil | | | | 72.00 | | | |
| Fatty monoglyceride | | •• | | - | | 16.00 | 16.00 |

The fatty monoglyceride is preferably cottonseed monoglyceride. These examples are used in oils or fats on the basis of from 0.005 to 0.02% of the di-tertiary-butyl-para-cresol. The amount of di-tertiary-butyl-para-cresol can be varied within these limits, maintaining the same proportions of propyl gallate, citric acid, and lecithin with respect to it which are shown in the above examples. The residue of the composition may then be made up with corn oil, assuming 8 ounces of the complete antioxidant composition for 1,000 pounds of lard or other fat or oil. Olive oil or cottonseed oil, lard oil, oleo, or other vegetable or animal oils may be used in place of the corn oil.

As an example of making the foregoing examples, anhydrous citric acid may be added to corn oil, previously heated to 265°F. The citric acid is added over a period of about 3 minutes and the mixture stirred continuously during this addition and for 45 minutes thereafter, until substantially complete reaction occurs. During this time, the temperature is maintained at about 265°F. The mixture is then cooled slowly to 120°F and agitation continued for about 20 minutes. The temperature is then raised to 160°F and the propyl gallate added with vigorous agitation for 15 minutes while maintaining the temperature at 160°F. After cooling to about 120°F, the di-tertiary-butyl-para-cresol is added, stirring slowly for about 20 minutes.

The citric acid and lecithin in Example 5 are incorporated as lecithin citrate in order to make the material oil and fat soluble. In Example 3 where propylene glycol is used as a solvent, the di-tertiary-butyl-para-cresol and butylated hydroxy anisole are dissolved in the propylene glycol with agitation at a temperature of approximately 120°F, together with the citric acid. In Example 4, the di-tertiary-butyl-para-cresol and butylated hydroxy anisole are dissolved in the lard oil with agitation at a temperature of 120° to 125°F. When tested with lard, the following improvement was obtained with respect to the AOM test and the Schaal Keeping Test.

| | AOM, hours | Schaal Keeping Test, days |
|--|------------|---------------------------|
| Control, no antioxidant | 4.5 | 17 |
| Di-tertiary-butyl-para-cresol, 0.01% | 13 | 27 |
| Di-tertiary-butyl-para-cresol, 0.02% | 20 | 27 |
| Control, no antioxidant | 6.5 | 17 |
| Di-tertiary-butyl-para-cresol, 0.005% | 20.0 | |
| Di-tertiary-butyl-para-cresol, 0.01% | 26.0 | 27 |
| Butylated hydroxy anisole, 0.01% | 27.0 | 31 |
| Di-tertiary-butyl-para-cresol, 0.015% | 34.0 | |
| Di-tertiary-butyl-para-cresol, 0.02% | 38.0 | 40 |
| Di-tertiary-butyl-para-cresol, 0.01% plus 0.003% citric acid | 30.0 | |
| Example 1 (8 oz/1,000 lb lard) | 41.Ú | |

BHA-BHT SYNERGISTIC COMBINATIONS

The process of L.R. Dugan, Jr. and H.R. Kraybill; U.S. Patent 2,926,092; February 23, 1960 is based on use of BHT (2,6-di-tertiarybutyl-p-cresol) and BHA (butylated hydroxyanisole) in combination with each other to produce a synergistic effect which greatly increases stability of animal fats and oils and greatly reduces and retards rancidity in foods containing such fats and oils.

To achieve an efficient and complete dissolution of the antioxidant additives in the glycerides, fats or oils, any desired proportions of 2,6-di-tertiarybutyl-p-cresol and butylated hydroxyanisole may be first dissolved in suitable mutual solvents such as propylene glycol, ethanol, and mono- and/or diglycerides, and/or triglycerides including animal fats and oils or mixed animal and vegetable fats and oils. The effective amount of 2,6-di-tertiarybutyl-p-cresol and of butylated hydroxyanisole will vary within the range from about 0.0005% to about 0.02% on a weight percent based on the amount of material to be stabilized.

The stability of a lard (Kingan lard) treated by adding to, separately and concurrently, nominal amounts of 2,6-di-tertiarybutyl-p-cresol and BHA. The AOM test was followed in all cases and the experimental results are tabulated as follows.

AOM Stability Induced by 2.6-Di-tertiarybutyl-p-cresol and BHA in Lard

| Antioxidant | Correlated AOM Stability (hr) | Difference from Control | Expected Stability Due to Components | Synergistic Effect (hr) |
|---|----------------------------------|-------------------------|--------------------------------------|----------------------------|
| Control (Kingan fard) | 11 | | | |
| 0.005% 2,6-di-tertiarybutyl- p-cresol | 37 | 26 | | - |
| 0.010% 2,6-di-tertiarybutyl- p-cresol | 53 | 42 | - | , |
| 0.020% 2,6-di-tertiarybutyl- p-cresol | 64% | 53% | | - |
| 0.010% BHA | 45% | 34% | - | - |
| 0.020% BHA | 54% | 43% | •• | |
| 0.005% 2,6-di-tertiarybutyl- p-cresol + 0.010% BHA | 80 | 69 | 60% | 8¼ |
| 0.010% 2,6-di-tertiarybutyl- p-cresol + 0.010% BHA | 101 | 90 | 76¾ | 13¼ |

The measured stability figures, listed in the second column, are obtained by a correlation of figures obtained from testing of several batches of the particular material. The Difference from Control column indicates the numerical difference in stability time directly attributable to the addition of the particular amounts of antioxidants. These figures are arrived at by subtracting the natural stability of the control (Kingan lard without additive) from the measured stability of the lard with the particular antioxidants incorporated.