

Light Stabilizers 2002  
An Intellectual Property Report

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## Introduction

This report is a summary and analysis of the intellectual property around light stabilizers, with particular reference to art that issued during 2002 and the first quarter of 2003. It is more directed towards use in a competitive analysis than, say prior art search for patentability, although it would provide a good start for a non infringement analysis. (Note that an accused product would have to be defined for the latter analysis to be derived from the present study. See [www.pearsonpatents.com/prior.htm](http://www.pearsonpatents.com/prior.htm) for a brief discussion on types of search.) Subsequent reports on the same subject will be issued annually, and will update the art for the prior year.

My objective is to provide inventors, management, and users in the art with an annual digest of the state of the art, in order to guide decision making processes.

This report is focused on U.S. patents. Relevant U.S. patents were selected using keyword combinations, and experimenting with those combinations until the number of patents yielded converges. The final keyword combinations arrived (which basically consisted of the the word “stabilization” in various forms with or without the assignees’ names) at could then used by the reader to expand the search to European and Wipo patents using, for example, [www.delphion.com](http://www.delphion.com).

The discussion is focused also on the claims of the patents, as the assignee can actually assert ownership of claims. (In some patents, in particular those that derive from divisionals or continuations, the title or abstract can actually be misleading as to what the claims contain.) It is not my intent to judge or comment upon the commercial value of any given patent or technology, so all patents are treated with equal reverence.

Commercial light stabilizers generally fall into one of two mechanistic classes, i.e. UV absorbers, and radical traps (hindered amines). However, in recent years these distinctions have become blurred by the promotion and use of blends of these classes, and also of blends with other additives, that are claimed in some cases to have benefits over single compounds.

In this study I have divided patents into those classes used by the USPTO and based on 35 U.S.C. to identify types of inventions. These would be compound patents for the material itself, and method patents for inventions that describe a means to stabilize a particular substrate. I have also introduced a “composition patent” type, that describes a polymer + additive combination that has a utility by virtue of its light stability, and a “mixture” patent type that corresponds to a mixture of stabilizers.

The final number of patents analyzed for this report was 56, with 41 going to Ciba, 7 to Cytec, 3 to Asahi Denka, and 4 to Great Lakes Chemical.

I felt that there were not enough patents in this field for a full fledged database to be worthwhile. The CD ROM that accompanies this report will have the images of the patents on it, and they can be read by the standard Windows® fax viewer, with some files being in Acrobat®'s "PDF" format.

The following aspects of the claims and disclosures are summarized:

Technology (type of compound.)

Statutory class (compound, "composition", method, "mixture".)

Substrate type (specific or general limitations on the polymer used if those limitations applied to the broadest claims.)

Examples (sometimes quoted if there are prominent examples that prove the utility of the invention.)

Priority date and continuation history (useful to gain an idea of when the development was being undertaken.)

The claim strategy behind most of the patents that we see here is to claim the invention as broadly as possible in the independent claims, often by not specifying in detail the polymers or processes that the stabilizer can be used with. The disclosure often lists substrates in more detail. The dependent claims are then narrowed to specific polymers and processes, in particular those that may appear described in more detail in the disclosure.

However, variations in the chemical structure that are possible while staying within the technology are often listed in great detail, even in the independent claims. (For example, Ciba's patents tend to be very specific in the disclosure and the claims about all of the possible variations of chemical structures that are available.)

It is not possible or worthwhile in a summary report such as this to simply list all of the limitations that are available publicly in the patent document itself. My intent here is to present a "big picture" view of where the intellectual property has been in the previous year, and what areas of chemistry appear to be engaging the R&D departments of the assignees in this technology.

Finally, note that in many cases more information about the scope of claims of any given patent can be gleaned from a study of the file wrapper, which can be obtained directly from the USPTO, or from any patent agency, including my own.

Please address all questions and suggestions to Tim Pearson at [mail@pearsonpatents.com](mailto:mail@pearsonpatents.com).

### Executive Summary

Somewhere around 70% of the patents issued in the period from 1/1/02 until 3/31/03 were assigned to Ciba. The others were split among Asahi, Cytec, and Great Lakes Chemical (GLCC) with one going to “others”.

Among Ciba patents, two technologies dominated. The first was the use of HALS “mixtures”. These patents had priority dates going back to the 1996 in some cases. The inventor was Gugumus. The HALS technology represented in these mixture patents was very broad, with polysilanes, and several products by process, and NOR HALS represented. In one case, mixtures of known commercial compounds could be identified. The utility of HALS is well known, and the advantages of these blends over single components would have to be understood from a more detailed reading of the examples, or from independent laboratory studies.

The second dominant technology from Ciba is the use of N-O-X-Y technology, where the Y group is electron withdrawing. (OH is an example). Several patents issued that were divisionals or continuations of U.S. 6,271,377, and covered compounds, compositions and methods for stabilizing. A common utility for all of these materials is efficacy in acid or other reactive environments. TPO’s, automotive coatings, and flame retarded systems are common examples and dependent claims.

Cytec now has NOR compounds patented also.

Ciba also claimed the rotomolding process with hydroxylamine stabilizers, the use of compositions that comprise metallocene polyolefins, and a process for stabilizing polyolefin moldings in permanent contact with water.

UV absorber technology is focused on reducing volatility (hydroxybenzophenones and benzotriazoles) and triazines for polymers that have a tendency to yellow on weathering (e.g. polycarbonate). All three of Ciba, Cytec, and Asahi Denka have carved out niches

with these molecules in terms of the substitution pattern on the triazine ring.

One note on “candle wax”. Ciba has several patents that claim stabilization of candle wax. In some cases they are very detailed (and some are recent enough to be included in next year’s report.) I have not included these patents here. They can be found easily enough at the USPTO’s search site by using the search string “an/ciba and candle”.

### Scope and Keywords

Searches in the USPTO database used the assignee name plus “stabilizer” or variants on it. (The names of the major assignees have not changed in the last two years, so for example use of the word “Cytec” does not have to be supplemented with “Cyanamid” as would be required if we were to go back (say) 20 years.)

Some patents, in particular for synthetic methods, will not reference the utility of the compound explicitly as “stabilization” so a check was run on some assignees to ensure that no method patents of this kind were missed.

All the information in this report is in the public domain, and nobody on the staff of any of the assignees was contacted to supplement the public information.

### Discussion by Technology

By “technology” I am referring to whether the compound in question is used as a UV absorber, a hindered amine radical trap, or something else.

Note that the technologies listed in this section are the dominant technologies in the patents – i.e. they appear in the independent claims. There may be dependent claims that further limit the invention to including other technologies. For example, a patent for a method of stabilizing a substrate may use a UV absorber in claim 1, and later include a HALS or a flame retardant with the UV absorber. The absorber, however, appears as a limitation in all claims. I do not mention the “secondary” technologies explicitly unless they appear to be critical to at least one independent claim, or have some other interesting characteristics..

#### *UV Absorbers - Benzotriazole or Hydroxybenzophenone*

The trend in UV absorbers is to increase the effective lifetime of the absorber in the polymer matrix by reducing volatility and susceptibility to heat degradation. There is also interest in protecting polymers that are intrinsically subject to discoloration (yellowing) on exposure to UV radiation.

#### **Ciba**

6,451,887 to Ciba is titled “Benzotriazoles containing a-cumyl groups substituted by heteroatoms and compositions stabilized therewith.” It claims **compounds**, very broadly benzotriazoles and oligomers, and **compositions** that comprise organic material and an

“effective amount” of the stabilizer. (You should expect to see “effective amount” defined somewhere in the disclosure.) Examples are given of photographic compositions, and PC and PMMA, in which inhibition of discoloration is an important utility.

A **composition** that contains a benzotriazole is claimed in U.S. 6,489,383 also to Ciba. This is a divisional of what became U.S. 6,392,056. The benzotriazole is substituted in the 5 position by a 1,1-diphenylalkyl group. Again, very broadly claimed, so an accused product would have to be read very carefully into the text of the claims. The disclosure specifically states the utility of this compound in automotive coatings. Examples include PC, PMMA and photographic materials. A high solids thermoset acrylic is given as an example of an automotive coating.

U.S. 6,392,056 (mentioned above) to Ciba has an abstract that describes the invention as:

“2H-Benzotriazole UV absorbers substituted at the 3-position or at the 5-position of the phenyl ring by a 1,1-diphenylalkyl moiety, particularly a 1,1-diphenylethyl group, are particularly photostable in automotive coatings, and are of low color and exhibit low volatility in thermoplastic compositions.”

The claims are for **compounds**. With variants of the title structure being described in detail in the claims.

U.S. 6,387,992 to Ciba claims as **compounds** substituted benzotriazoles and also a process for preparation of the compounds. Compositions are claimed, in particular with coatings, polyester, PU. This one was filed 11/27/2000.

U.S. 6,458,872 to Ciba is a divisional of a divisional that became U.S. 6,262,151, which is a divisional of U.S. 6,166,218, which is a continuation-in-part of application Ser. No. 08/961,127, filed on Oct. 30, 1997, now U.S. Pat. No. 5,977,219. A **composition** is claimed that is stabilized against thermal, oxidative or light-induced degradation which comprises an organic material selected from the group consisting of a thermoset acrylic melamine resin, an acrylic urethane resin, an epoxy carboxy resin, a silane modified acrylic melamine, an acrylic resin with carbamate pendant groups crosslinked with melamine or an acrylic polyol resin crosslinked with melamine containing carbamate groups, and an effective stabilizing amount of a compound. The compounds of the abstract are benzotriazole UV absorbers which are substituted at the 5-position of the benzo ring by an electron withdrawing group.

6,495,622 to Ciba (filed 11/27/2000) claims **compositions** that comprise polyolefins and a stabilizer that is a dimeric hydroxybenzophenone. Persistency of the additive in film is one goal (utility) for the invention. A method for stabilizing is also claimed. The example

in the disclosure of stabilization is a LDPE film.

U.S. 6,515,051 to Ciba has a divisional history going back to 6,262,151, 6,166,218, and 5,977,219. A composition that comprises organic material and an effective amount of stabilizer is claimed. Cyano or perfluoroalkyl substituents on a benzotriazole backbone(s) seem to be the core of the claims. It is titled "Benzotriazole UV Absorbers having Enhanced Durability."

U.S. 6,369,267 to Ciba is a divisional of a now abandoned U.S. application (09/214,859) and that was a European application. The original application was filed 7/7/97. It is essentially a compound patent for a bis hydroxybenzophenone. I was unable to find another U.S. patent that referenced that application number.

### **Cytec**

Cytec has 6,537,670 (filed 11/3/2000) which claims as a **compound** bis benzophenones with various substitutions. Also a process for preparing from hydroxyhydrocarbyl functional benzophenones. Polymeric articles that contain the stabilizer are also claimed. Quote from the disclosure.. "Therefore a need remains for compositions that stabilize polymeric materials against degradation caused by exposure to UV light, while simultaneously demonstrating low volatility, low color and high solubility. The present invention provides such compositions."

U.S. 6,344,505 to Cytec claims a composition, that comprises mono- or bis-benzotriazolylidihydroxybiaryl absorbers. This composition is then claimed later in combination with degradable polymers. Filed 11/11/99.

### **Great Lakes Chemical**

Great Lakes Chemical claims a **compound** 2-(2'-hydroxyphenyl) benzotriazole in U.S. 6,407,254. A **process** for making this material is also claimed. The inventor discloses that the claimed structure overcomes disadvantages with known art that include high volatility and susceptibility to thermal degradation. Many polymers and coadditives are disclosed but not claimed for use with this material.

Great Lakes also has a patent (U.S. 6,403,679) on a granular **mixture** of a nickel quencher and a specific hydroxybenzophenone (2-hydroxy-4-n-octyloxybenzophenone).

Agricultural films and methods for stabilizing them are also claimed, as are greenhouses that use the films.

U.S. 6,452,018 is titled "2-(2'-hydroxyphenyl) benzotriazoles containing a 2,4-imidazolidinedione group and process for their preparation". It has European priority back to 1998. The claim is for a compound that is a dimeric benzotriazole. A process for preparation of these compounds is also claimed. A quote from the patent disclosure as to utility:

"The Applicant has now surprisingly found that 2-(2'-hydroxyphenyl)benzotriazoles containing a 2,4-imidazolidinedione group or a 2,4-imidazolidinedione-5,5-disubstituted group in the molecule, are capable of overcoming the drawbacks of the known art. In fact, the above benzotriazoles have a low volatility (they are therefore able to remain inside the stabilized organic polymer for a longer period) and also a high thermal stability. In addition, they have a low absorption ("cut-off") at  $[\lambda]=400$  nm and an excellent absorption at  $[\lambda]=302$  nm and at  $[\lambda]=340$  nm and consequently they do not give a yellow colouring to the polymers into which they are incorporated."

#### *UV Absorbers - Triazine*

Recently issued patents seem to claim for the most part stabilized compositions or methods for stabilizing. The presence of divisionals indicates that restriction requirements were required on the original applications, which probably went on to become the compound patents. Ciba has the bulk of the patents, and the emphasis seems to have been in covering the substitution pattern on the triazine ring.

#### **Ciba**

**Compositions** containing triresorcinol triazines are claimed in U.S. 6,509,400 (to Ciba), which is a divisional of U.S. 6,346,619 (filed 5/3/99). The compositions claim "organic material" and stabilizer. The latter patent is for the compound.

Substituted trisaryl triazines are used in a **method** to stabilize materials and protect films and coatings in U.S. 6,365,652 to Ciba. (An example material that is given is PU.) This is a divisional of what became U.S. 6,265,576, and the provisional on which they were based was filed in 1997.

U.S. 6,355,708 to Ciba claims a **method** for stabilizing (and later a coating composition)

that uses a “bondable” trisaryl-1,3,5-triazine. “Bondable” refers to the ability of the stabilizer to bond to the polymer substrate. This is a divisional of what became U.S. 6,242,597, and is also based on a provisional filed in 1997.

U.S. 6,468,958 to Ciba is a **compound** patent for a biphenyl substituted triazine compound. It is a divisional of U.S. 6,255,483, which claims priority via a continuation to 9/10/97. One of the substituents can also be a 2,2',6,6'-tetramethyl piperidinyl ring. Four of the claims are also directed to a method for increasing the sun protection factor of textile materials by applying the compound.

U.S. 6,486,317 claims...

### **Cytec**

U.S. 6,509,399 to Cytec claims a **method** to stabilize a material using para tert alkyl phenyl substituted triazine and pyrimidine UV absorbers. It is a division of what became U.S. 6,239,276, and the provisional filing was on 6/22/98 and 11/17/98. (Note also that one inventor seems to be inventing for Ciba also now.) The title of this patent asserts the property “non yellowing” and there are examples of applications in PC and melamine coatings.

U.S. 6,384,113 to Cytec claims a **composition** that comprises a benzocycle substituted triazine or pyrimidine of the title, plus another stabilizer (light stabilizer, UV absorber or antioxidant.) A later claim then goes on to add a polymer to the composition. This patent is a divisional of what became U.S. 6,297,377, filed on 8/10/01, and based on a provisional going back to 1998.

### **Asahi**

Other triazine patents going to Asahi are U.S. 6,333,114 triazines for PC (issued 12/25/01) and U.S. 6,500,887. The former would be considered a **composition** patent here, but actually claims a coextruded article which has one layer of PC with a specific trisaryl triazine. All claims except claim 1 are dependent.

U.S. 6,500,887 claims a composition for a polymeric material plus a triazine compound. PC and PMMA are claimed specifically in dependent claims.

### *Hindered Amines*

As mentioned above, I have included another type of composition in this discussion –

namely “mixtures”. This is because many of the patents that were issued to Ciba during 2002 and early 2003 were for mixtures of hindered amines, a technology that Gugumus has been the inventor on most of the patents. If any NOR type HALS appear in the independent claims, then I have included the patent in that category, even if it includes claims for NH type HALS also.

Other than mixtures, the other technology with a large number of patents is Ciba’s N-E-OH or N-E-OR technology. Most of the patents in this area are divisionals or continuations of a parent – U.S. 6,271,377, which I will describe even though it falls outside of the scope of the time range of this study.

#### *Conventional NH or NR Technology*

### **Ciba**

Stabilizer mixtures are popular this year, with Gugumus having a number issued based on work presumably carried out in the 1990’s, looking at the priority dates. The first three patents mentioned below claim compositions that comprise a product by process.

Two patents claim **mixtures** or **compositions** that comprise polysilanes. U.S. 6,328,912 is a mixture of components, namely a polysilane with pendant hindered piperidine groups, a product by process, and other coadditives (notably magnesium oxide and hydroxide) and a UV absorber and/or a pigment. Foreign priority goes back to 7/12/96. Examples in the disclosure include use in PP.

In U.S. 6,365,651 to Ciba one of the compounds claimed is an NO radical. All the others are NH. This is a **mixture** patent to Ciba (Gugumus) and a divisional of what became 6,020,406. Priority goes all the way back to 2/5/96. It is for a composition, and one component is a polysilane with pendant hindered piperidine groups. One component is a product by process (i.e. it is defined by what you get when you react certain things together.)

U.S. 6,380,286 to Ciba is a Gugumus **mixture** patent. It claims a mixture that comprises a material that has the hindered N moiety in the oligomer chain, and it comprises also a **product by process**. This is a divisional of what became 6,015,849 and the original filing (of an abandoned application) was in 1996. A composition with an organic material, and a process for stabilizing are also claimed.

U.S. 6,545,071 to Ciba is another Gugumus **mixture** patent. The mixture comprises an

N-R-N type HALS dimer, with a NH or NR type HALS, and a UV stabilizer and / or pigment. A composition for the mixture plus a PO is claimed. Filing date was 8/14/97.

U.S. 6,403,680 to Ciba is one of a long list that issued in this time period that shows Galbo as first inventor. This is a compound patent that is for a product by process. A stabilized composition is claimed, as is a method of stabilizing organic material. The process begins with a tri substituted triazine and ends with an oligomeric material. PCT was filed 5/14/99.

A stabilizer **compound** is claimed in U.S. 6,416,627 to Ciba. The stabilizer comprises a polymer with pendant groups which are attached in turn to the polymer by bridging groups. The stabilizer is also claimed as a reaction product. A **process** is also claimed for stabilizing paper or pulp against discoloration.

### **Cytec**

U.S. 6,414,155 to Cytec claims a **compound** and a **method** for forming the compound. The compound is described in the title as a hindered amine derived from multifunctional carbonyl compounds. The N-R group of the hindered amine appears in the oligomer backbone. Examples include stabilization of acrylic urethane clear coat compositions. Filing date was 11/3/00.

6,492,521 to Cytec is a CIP of the '155 application. It is also a **compound** patent, for a similar type of structure.

### **Great Lakes Chemical**

Great Lakes also has a patent (U.S. 6,353,044) that is for a **composition** of an organic material and a hindered amine  $\beta$ -(2,2,6,6-tetramethylpiperidine-4-amino) ethyl crotonate. Note that the patent is subject to a terminal disclaimer, which may mean that there is a similar GLC patent somewhere with essentially the same invention claimed. A reading of the file wrapper would confirm this.

### *NOR and other Technologies*

The dominant technology in this section is the NOR technology derived from U.S. 6,271,377. The table in the appendix summarizes some of the relationships among these patents.

## Ciba

### *Derivatives of U.S. 6,271,377*

U.S. 6,271,377 appears before the time scope of this report, however, many of the patents that issued this year derive from it, so it deserves to be mentioned here. It claims a compound having 1-alkoxy substituted hindered amine derivatives where the alkoxy moiety is substituted by one to three hydroxy groups. Formulae then describe the covered compounds in the first and seven dependent claims. No other compositions or methods are claimed.

U.S. 6,391,949 to Ciba claims **compositions** that include organic polymer and –N-O-G-Acyl structures, where G is alkylene. It is a division of what became 6,271,377 which was filed on 2/22/01. The utility disclosed in these patents seems to be generally good performance in acid coating environments, and in the presence of halogenated flame retardents.

6,376,584 to Ciba is a **compound** and **composition** patent. It claims 1-alkoxy bridged HALS derivatives. Structures are specified very closely. Two or three hindered amine molecules share the alkoxy bridges with –OH groups. Compositions with organic polymer are also claimed, with film, fiber, thick section and coadditives and costabiizers being specified, including flame retardents and pesticides. A mixture of compounds with a product by process is also claimed. Examples include PP and TPO based materials, and acrylic urethanes. This patent is a CIP of a CIP back to US 6,271,377, with a priority date of 2/25/99.

U.S. 6,388,072 is a **compound** patent. It claims a compound with a N-O-L-(OH)<sub>6</sub> type of structure at the hindered amine. Many examples are cited, with compositions that contain flame retardants and coatings being important utilities for the invention.

U.S. 6,392,041 is also a **compound** patent. The compound is a trimer of a hindered piperidine with a N-O-E-(OH)<sub>6</sub> structure, and E is an alkylene group, broadly defined and claimed. Coatings and flame retarded hydrocarbon polymers are again the focus of the utility of the invention.

U.S. 6,403,681 to Ciba claims **compositions** comprising organic polymer + 1-alkoxy substituted HALS with OH substitution (i.e. N-O-E-(OH)<sub>6</sub>). It is a divisional of what became U.S. 6,271,377.

U.S. 6,420,562 claims a **product** by process that is a condensation product of a dialkyl

ester or diisocyanate with an N-alkoxy derivative of a hindered piperidine.

U.S. 6,420,463 to Ciba is a divisional of what became 6,271,377. This patent claims a **composition** that comprises an organic polymer with an effective stabilizing amount of the product of a condensation reaction (i.e. a product by process). The claims then go on to limit the first claim with other additives.

U.S. 6,380,389 is a divisional of U.S. 6,271,377 and claims a compound which is a diester or urethane derivative of a hydroxy substituted N-alkoxy derivative of 4-hydroxy-2,2,6,6-tetramethylpiperidine.

#### *Other NOR Type*

U.S. 6,409,941 to Ciba claims a **product** by the process of transforming NH to NOR groups. . The subject NH molecule looks very similar to Ciba's Chimassorb® 944. Also claims a mixture of three monodisperse oligomers within certain ratio limits. Also a method for stabilizing an organic material. Also a composition that comprises the mixture and an organic material. The title is "Block oligomers containing 1-hydroxycarbyloxy-2,2,6,6-tetramethyl-4-piperidyl groups as stabilizers for organic materials." The PCT for this patent was filed 5/14/98.

U.S. 6,403,680 was also filed as a PCT on 5/14/98. It also claims a product by process. A series of reaction steps yields an NOR HALS. Compositions with organic materials are also claimed.

U.S. 6,368,520 is another Gugumus **mixture** patent. Which is a divisional of what became 5,980,783. Priority goes back to 1995. The mixture is of NOR HALS, and compositions with organic materials are also claimed.

U.S. 6,420,462 is a Ciba patent that is titled as a method of preparation, but actually claims a **composition** with an organic polymer and an amine ether. It also claims a process for either stabilizing or flame retarding an organic material. It is a continuation of a patent that was filed on 2/19/99, namely 6,117,995.

U.S. 6,441,166 is a **mixture** patent. Many mixtures and claimed, with some being the results of processes. The provisional to which this patent claims priority was filed in 12/98.

U.S. 6,465,645 claims **compounds**. They are NOR or NOE(OH)<sub>6</sub> HALS, with triazine rings attached to the piperidine group, sometimes via a bridging atom or group. Candle wax is quoted extensively in the examples, and the title and abstract invoke the idea of a long hydrocarbon chain as an improver of solubility in an organic matrix. No compositions are claimed.

### **Cytec**

U.S. 6,545,156 is assigned to Cytec. It claims as compounds oligomeric HALS that can be NR, NO, NOH or NOR. A process for preparation is also claimed. Good YI performance is disclosed in nylon. PP and various other polymers are also disclosed.

### *Other Technologies*

3-arylbenzofuranones are claimed as stabilizers by Ciba in U.S. 6,346,630. The divisional history of this one goes back to US patents 5,814,692, 5,773,631, and 5,516,920. The claims are for the compounds, compositions comprising organic material that is subject to thermal or light induced degradation. A method for stabilizing is also claimed.

BASF has a patent (U.S. 6,492,442) that claims a **composition**. The composition comprises four components. One is a 3-arylacrylic ester, one is a polymer carrying side groups with secondary amine functions, one is a "chroman" derivative, and one is an organic phosphite or phosphonite. Note that all four of these components have to be present in the invention. A further claim is for a method to stabilize an organic material using this composition, and polyurethanes are specified in an independent claim.

### Process and Substrate Specific Patents

#### **Ciba**

U.S. 6,444,733 to Ciba falls into this category. It is a CIP of 09/259,724 from 3/1/99. It claims the rotomolding process in which a phosphite + a hindered amine + a hydroxylamine derivative is used to stabilize the polymer.

6,521,681 to Ciba has a filing date going back to 6/23/97 and a foreign priority to 7/5/96. It claims phenol free stabilization of polyolefins. A composition is claimed that

comprises a PO, a benzofuran-2-one type of compound and a hindered amine. (Phosphites are added in a later, dependent claim.) I have mentioned it in this section as it is titled "polyolefin fiber..." although note that the claim is broader than the title.

6,512,029 to Ciba (Gugumus is inventor) claims stabilization of metallocene polyolefins. This patent has no divisional or continuation history, and was filed 1/27/2000. The European priority date was 2/1/99. The first claim is for a composition containing a PO prepared over a metallocene catalyst, and a stabilizer mixture comprising two out of three types of hindered amine compounds. (The easiest way to think of this mixture from a commercial point of view is as a mixture of two out of three of Chimassorb® 944, Tinuvin® 622 and /or Chimassorb® 119 and variants of the three.)

6,541,547 to Ciba claims a process for stabilization of polyolefin moldings in permanent contact with water. A combination of a phosphite, a hindered phenol and a HALS of molecular weight greater than 1000 is used. The filing date for this patent was 9/9/96. The patent term was extended as a result of the long prosecution time.

### **Asahi**

Asahi Denka claims a composition that includes a hindered piperinidyl (nitroxyl) radical for use in agricultural film applications in U.S. 6555603. Although note that the limitation to agricultural film does not appear in the body of the claim (it is in the preamble) so it may not be a limitation of the claim.

## **APPENDICES**

Other Numbers of Interest.

Table of Derivatives of U.S. 6,271,377

List of Patents Cited.

**Other Patents.**

Other numbers of interest but that fall outside of the time scale of this study or may have been quoted as related to divisionals or continuations are:

Triazines

6,306,939 to Ciba, Issued 10/21/01.

6,255,483

6,284,821

Benzotriazoles

6,515,051 and 6,458,872 to Ciba

see

6,262,151

6,166,218

5,977,219

**THE DERIVATIVES OF U.S. 6,271,377**

Number	Filing Date	D, C or CIP	Type and Content of Claims
6,271,377	2/25/99		A compound having 1-alkoxy substituted hindered amine derivatives where the alkoxy moiety is substituted by one to three hydroxy groups.
6,376,584	2/27/01	CIP	<p>A compound having 1-alkoxy bridged hindered amine derivatives where the alkoxy moiety, substituted by one to three hydroxy groups, is shared by two or three non-equivalent hindered amine molecules.</p> <p>Or novel compounds having 1-alkoxy bridged hindered amine derivatives where the alkoxy moiety, substituted by one to three hydroxy groups, is shared by three hindered amine molecules.</p> <p>A composition which comprises an organic polymer or recording material subject to the adverse effects of heat, oxygen and light, and an effective stabilizing amount of one or more compounds selected from the compounds of the earlier claims.</p>
6,380,389	2/21/01	D	A compound which is a simple diester or urethane derivative of a hydroxy substituted N-alkoxy derivative of 4-hydroxy-2,2,6,6-tetramethylpiperidine.
6,388,072	2/21/01	D	A compound having 1-alkoxy bridged hindered amine derivatives where the alkoxy moiety, substituted by one to three hydroxy groups, is shared by two hindered amine molecules.
6,391,949	2/22/01	D	A composition which comprises an organic polymer subject to the adverse effects of heat, oxygen and light, and an effective stabilizing amount of a compound which is a simple diester or urethane derivative of a hydroxy substituted N-alkoxy derivative of 4-hydroxy-2,2,6,6-tetra-methylpiperidine.

6,392,041	2/17/00	D	A compound that is a trimer of a hindered piperidine with a N-O-E-(OH) <sub>b</sub> structure. E is an alkylene group.
6,403,681	2/21/01	D	Compositions of the compound of 6,392,041.
6,420,562	2/21/01	D	A compound of which is the condensation product of a dialkyl ester or diisocyanate with a hydroxy substituted N-alkoxy derivative of 4-hydroxy-2,2,6,6-tetramethylpiperidine.
6,420,463	2/21/01	D	A composition which comprises an organic polymer subject to the adverse effects of heat, oxygen and light, and an effective stabilizing amount of a compound of 6,420,562.

D = Divisonal (i.e. the same disclosure was used for claims to a new invention),  
 C = Continuation (i.e. no new matter was added relative to the parent),  
 CIP = Continuation in Part (i.e. some new matter was added, and receives a later priority date).

**Patents Cited**

Ciba

<b>Chemical Type</b>	<b>Numbers</b>
Hydroxybenzophenones	6,495,622; 6,369,267;
Benzotriazoles	6,387,992; 6,392,056; 6,451,887; 6,458,872; 6,489,383; 6,515,051;
Triazines	6,306,939; 6,346,619; 6,355,708; 6,365,652; 6,468,958; 6,509,400;
NH or NR HALS	6,328,912; 6,365,651; 6,380,286; 6,403,680; 6,416,627; 6,444,733; 6,512,029; 6,521,681; 6,545,071; 6,541,547;
NOR(OH) HALS	6,271,377; 6,376,584; 6,380,389; 6,388,072; 6,391,949; 6,392,041; 6,403,681; 6,409,941; 6,420,463; 6,420,562; 6,465,645;
NOR HALS	6,368,520; 6,403,680; 6,409,941; 6,420,462; 6,441,166;
Other	6,346,630;

Total : 41

Cytec

<b>Chemical Type</b>	<b>Numbers</b>
Hydroxybenzophenones	
Benzotriazoles	6,344,505; 6,537,670;
Triazines	6,384,113; 6,509,399;
NH or NR HALS	6,414,155; 6,492,521;
NOR(OH) HALS	
NOR HALS	6,545,156;
Other	

Total : 7

Asahi

Chemical Type	Numbers
Hydroxybenzophenones	
Benzotriazoles	
Triazines	6,333,114; 6,500,887;
NH or NR HALS	
NOR(OH) HALS	
NOR HALS	
Other	6,555,603;

Total : 3

Great Lakes Chemical

Chemical Type	Numbers
Hydroxybenzophenones	6,403,679;
Benzotriazoles	6,407,254; 6,407,254;
Triazines	
NH or NR HALS	
NOR(OH) HALS	
NOR HALS	
Other	6,353,044;

Total = 4

Others

<b>Chemical Type</b>	<b>Numbers</b>
Hydroxybenzophenones	
Benzotriazoles	
Triazines	
NH or NR HALS	
NOR(OH) HALS	
Other	6,492,442