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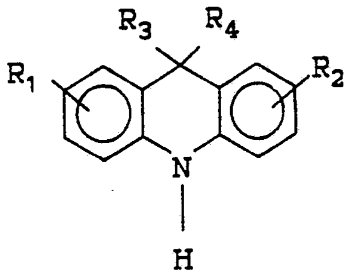

(I)

(57) Abstract

The invention relates to the use of an acridans of structure (I) as a stabilizer, preferably combined with hindered amine, phenolic, and phosphite stabilizers for stabilizing polyether polyols for polyurethane flexible foams and as stabilizers for the polyglycols, heat transfer fluids, lubricating additives.

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STABILIZATION OF POLYOXYALKYLENE POLYETHER POLYOLS

FIELD OF THE INVENTION

The present invention relates to the stabilization of polyoxyalkylene polyether polyols and the use of the stabilized polyols in the preparation of polyurethane foam. In particular the invention relates to stabilization of polyols with certain stabilizer compositions and the color stability or scorch inhibition of flexible and semiflexible polyurethane foams made from the stabilized polyols.

BACKGROUND AND RELATED ART

Prior art methods for the stabilization of polyalkylene polyether polyols with antioxidants or stabilizers and the use of stabilized polyols in the preparation of polyurethane foams to inhibit scorch are well known. Polyether polyols, used in the manufacture of slabstock flexible urethane foam, are typically stabilized with antioxidant packages consisting of phenolic and amine antioxidants, and may also contain the synergist phenothiazine.

United States Patent Nos. 3,567,664 and 3,637,865 disclose polyurethane foams stabilized with a mixture of 2,6-di-tert-butyl-4-methyl phenol [butylated hydroxy toluene (BHT)] and p,p'-dialkyldiphenylamines. United States Patent No. 4,010,211 teaches the addition of phenothiazine to a BHT/p,p'-dialkyldiphenylamine mixture. United States Patent No. 4,794,126 discloses flame-retardant polyurethane foams stabilized with a combination of a diarylarylenediamine, a reaction product of diarylamine and alkyl ketone and a hindered phenol, specifically 3,6'-di-tert-butyl-4-sec-butyl phenol.

United States Patent No. 4,933,374 discloses polyoxyalkylene polyether polyol compositions protected against oxidative degradation with a stabilizing amount of a synergistic mixture of 2,6-di-tert-butyl-4-sec-butyl phenol and a reaction product of diisobutylene, styrene, and diphenylamine wherein the weight ratio of the diisobutylene to the styrene is from about 2:1 to 5:1.

United States patent 4,551,493 is concerned with transparent flame-retardant poly(arylether-arylsulfone) molding materials. An example of a heat stabilizer given is a hindered phenol and a diphenylamine/acetone condensate. In this patent, the final product is used as a flameproofing agent for plastic molding materials. Certain simple acridan compounds of the instant invention are disclosed but not exemplified as useful in stabilization of the sulfur bearing poly (aryletherarylsulfone) polymers. Furthermore, the cyclic or linear diphenylamine/acetone condensate of US 4,551,493 are used in combination with a poly(2,6-dibromophenylene 1,4-oxide). The compositions of the instant invention are not halogenated in any manner nor do the stabilized polymer chains contain a sulfur linkage.

Antioxidants are used in polyether polyols to protect the polyol from oxidation during the final stages of manufacture; to reduce peroxide formation during storage; and to reduce the possibility of scorching the flexible polyurethane slabstock foam due to thermal oxidative degradation.

The compounds of this invention are particularly important to the polyol/flexible urethane industry due to the increased concern over chlorofluorocarbons (CFCs) and their deleterious effect on the earth's ozone layer. CFCs are incorporated in flexible slabstock foam to serve as an auxiliary blowing agent and for the removal of heat during slabstock production. The absence of CFCs places a higher performance requirement on the stabilization system, since the CFCs prevent discoloration, physical scorch and self-ignition of the foam.

The presence of scorch is of major concern to the foam manufacturers since it negatively affects the appearance of the product, causes physical damage and may result in fire. Recent regulations eliminating the use of CFCs in polyurethane foam manufacture require enhanced scorch protection during flexible slabstock foam production.

It would therefore be advantageous to have a antioxidant system for polyether polyol stabilization that provide increased scorch protection, allow foams to be produced at higher internal temperatures, and eliminate the use of CFCs without adverse effects to the foam.

Accordingly, it is an object of this invention to provide a stabilizer system for polyether polyols which provides valuable protection for oxidation, scorching, and discoloration of resultant foam produced, including those foams produced containing flame retardants.

It is a further object of this invention to provide an environmentally friendly stabilization package for polyether polyols. More specifically, a stabilization package which holds the possibility of eliminating the need for chlorofluorocarbons, heretofore used in flexible polyurethane foam production.

It is a still further object of this invention to provide a flexible polyurethane foam product made from the stabilized polyol together with an isocyanate with improved scorch performance, appearance, and color.

The foregoing and additional objects will become more evident from the following description and Examples.

SUMMARY OF THE INVENTION

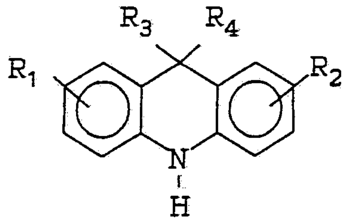
The stabilizers of the instant invention is comprised of a class of amine stabilizers, known as acridans, which shows efficacy as well as unexpected synergy when combined with traditional amine, phenolic, phenothiazine and phosphite stabilizers in stabilizing polyether polyols for polyurethane flexible foams which may contain flame retardants as well as other non-sulfur contained polymers subject to heat and oxidane degradation.

Another aspect of this invention concerns a method for the stabilization of polyalkylene polyether polyols against oxidative degradation and the use of such a stabilized polyol together with polyisocyanates to prepare scorch stabilized polyurethane foams.

Yet another aspect of this invention concerns a method of stabilizing polyglycols, heat transfer fluids, lubricating additives, and the like using the synergist of this invention with traditional stabilizers to increase the efficacy of the stabilizer system and enhance the properties of the respective products.

DETAILED DESCRIPTION OF THE INVENTION

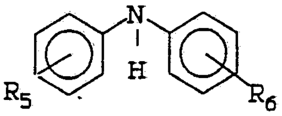
In one aspect, the instant invention is directed to the use of:



I

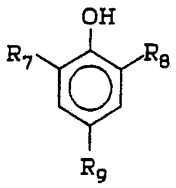
wherein R_1, R_2, R_3, R_4 can be H, C_1-C_{18} alkyl, or C_7-C_{18} aralkyl. R_3 and R_4 can also be aryl, preferably phenyl.

The term, "acridan", as depicted in structure I above will be used hereinafter to refer to the group of compounds structurally represented by (I). The acridan may be optionally combined with an amine stabilizer of the structure II



II

wherein R_5 and R_6 can be H, C_1-C_{18} alkyl, C_7-C_{18} aralkyl, a phenolic stabilizer of structure III

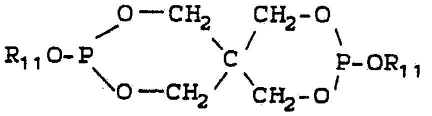


III

wherein R_9 can be C_1-C_{18} alkyl or C_7-C_{18} aralkyl and R_7 and R_8 are C_4-C_{12} alkyl, C_7-C_{12} aralkyl, preferably t-butyl; or optionally combined with a phosphite stabilizer of the formulas IV or V.

$(R_{10}O)_3$-P

IV



V

wherein R_{10} and R_{11} are independently selected from C_6-C_{18} alkyl, aryl, C_7-C_{18} aralkyl, or C_7-C_{18} alkaryl.

Examples of such known stabilizing amines, phenols, and phosphites include dioctyl diphenylamine, butylated hydroxytoluene, (2,6-di-t-butyl-4-methylphenol), phenothiazine, 4,4'-bis(alpha,alpha-dimethylbenzyl) diphenylamine, styrenated diphenylamines, diisobutylated diphenylamines, mixtures of styrenated and diisobutylated diphenylamines, mixtures of styrenated and α,α,dimethylbenzyl diphenylamines, mixtures of butyl, dibutyl, and octyl diphenylamines, dimerized 2,2'-methylene bis-6-t-butyl-p-cresol, 2,6-di-t-butyl 4-sec-butylphenol, tris(nonylphenyl) phosphite, tris(2,4-di-t-butylphenyl) phosphite and the like.

Preferred substituents of Structure I include those when R_1 and R_2 are hydrogen and R_3 and R_4 are alkyl. A more preferred substitution would include R_1 and R_2 as hydrogen and R_3 and R_4 as methyl.

A preferred amine compound for the stabilizer package of this invention includes structure II above wherein R_5 and R_6 are α,α,dimethylbenzyl.

A preferred phenolic stabilizer of this invention includes structure III above wherein R_9=sec-butyl or methyl and R_7 and R_8 are t-butyl.

The stabilizer system containing an acridan along with currently used commercially available stabilizers will contain from 1 to 50% by weight of the acridan component in the polyether polyol stabilizer system. A preferred range is from 2 to 20% by weight of the acridan component in the polyether polyol stabilizer system. A most preferred range is from 2 to 10% by weight of the acridan component in the polyether polyol stabilizer system.

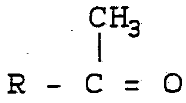
In another aspect, this invention relates to the manufacture of flexible polyurethane slabstock manufactured from polyether polyols stabilized by the compositions described herein.

Among the commercially available amine and phenolic antioxidants utilized in the compositions of this invention are known by several trademarks including Naugalube™ 680, 635 or 640, Naugard™ 445; Naugard™ BHT, PS-20, PS-30; (trademarks of the Uniroyal Chemical Company), Isonox™ 132 (trademark of Schenectady Chemical Company) and others. Other commercially available antioxidants considered to be within the scope of this invention include phenothiazine, phosphites, bisphenols, and the like. These type products are well-known and familiar to those skilled in the art. Acridans provide increased performance in systems where simply increasing antioxidant levels shows little or no increase in performance.

SYNTHESIS OF THE ACRIDANS

The acridan component of this invention was synthesized by the following procedure: The low temperature reaction product of diphenylamine and acetone is synthesized according to U.S. Patent 2,202,934 (available as Aminox™ from Uniroyal Chemical Company) and 3% by weight iodine were heated to 240°C for four hours. The crude reaction mixture, which contained diphenylamine, dimethylacridan, isopropyl diphenylamine, and dimers and trimers of various alkylated diphenylamines, was carefully fractionally vacuum distilled. The portion boiling at 130-140° C at 0.3 mm Hg was collected. The desired product, 9,10-dihydro-9,9-dimethylacridan (abbreviated a AC1 in Table 1), was recrystallized from hexanes. The product yield was < 30%.

Other acridans of Structure (I) are made by an analogous reaction of a p-di-alkylated diphenylamine with a ketone where the alkyl substituents of the DPA are R_3 and R_4 and the ketone is of the form



$$\begin{array}{c} \quad CH_3 \\ \quad | \\ R - C = O \end{array}$$

where R is C_1-C_{18} alkyl, or aryl, alkaryl (C_7-C_{18}) or C_1-C_{18} aralkyl of Structure I and other synthesis techniques and routes can be contemplated to produce improved selectivity and yield.

Synthesis of AC2 and AC3 referring to Structure I, the compound referred to hereinafter as AC2 has the following representative structure: R_1, R_2 are t-octyl, R_3 is phenyl and R_4 is methyl. AC3 compound has R_1 and R_2 = t-butyl, R_3 is phenyl and R_4 is methyl.

A di-p-t-octyl-diphenylamine was reacted with acetophenone to form the acridan AC2; in the case of AC3 di-p-t-butyl diphenylamine was reacted with acetophenone.

This AC2 and AC3 compounds demonstrated excellent utility although AC1 is slightly superior; therefore, AC1 is highlighted in the subsequent comparisons with commercial control stabilization systems.

STABILIZER PACKAGE PREPARATION

The acridan component of the stabilizer package was combined with commercially available amine and phenolic stabilizers including dioctyl diphenylamine (abbreviated as dioctyl DPA), 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT), phenothiazine (PTZ), 4,4'-bis (alpha,alpha-dimethylbenzyl)-diphenylamine (also known as Naugard 445 and abbreviated in Table 1 as 445), 2,6-di-t-butyl-4-sec-butylphenol (also known as Isonox 132 and abbreviated as 132), a mixture of styrenated/diisobutylated diphenylamine.(also known as Naugalube 680) according to the amounts listed in Table 1. Each combination was tested for polyether polyol stabilizer performance.

EXAMPLES

TABLE 1

Example	A	B	C	D	1	2
Component						
Dioctyl.DPA	2200	1950	-	-	-	-
BHT	2200	2150	2200	2150	-	2150
PTZ	-	100	-	100	-	-
445	-	-	2000	1950	-	1950
680	-	-	-	-	1950	-
132	-	-	-	-	2150	-
AC1	-	-	-	-	100	100

In order to demonstrate the effectiveness of the stabilizer systems of this invention, they were evaluated against commercial antioxidant stabilizer packages. Both the commercial and experimental types of stabilizer systems are listed in Table 1. All of the antioxidant packages were loaded into 3,000 average molecular weight polyol at levels typically used by the major polyol producers, ranging from 0.2 to 0.7 weight percent.

The polyols used in these tests were selected from the commercially available polyols Voranol™ 3137 (trademark of the Dow Corporation) or Niax™ 16-52 (trademark of the Union Carbide Corporation). The average molecular weight of these materials is approximately 3000.

The polyether polyols that were stabilized by these stabilizer systems indicated in Table 1, were tested by differential scanning calorimetry (DSC), thermogravimetrically analyzed (TGA) and APHA color tested. The procedures and results of these tests are given below.

TGA METHOD/ANALYSIS

Thermogravimetric analysis measures the dynamic relationship between the temperature and the mass of a system. By comparing the mass of a sample to that of a controlled system, the temperature at which weight loss is experienced due to evaporation, decomposition, or combustion may be determined.

In this evaluation, a sample weighing approximately 30 mg was placed in the sample chamber of a Perkin-Elmer TGS-2 Thermo Gravimetric Analyzer. The chamber was then equilibrated, under nitrogen, to 130°C. Once equilibrated, the gas in the sample chamber was switched from nitrogen to air at a flow rate of 100 cc/min and the temperature ramped at 5°C/min until 100% weight loss of the sample had occurred. Although actual foam formulations contain many components which are not present in the TGA test, it is considered an excellent means for initial screening of antioxidant candidates. The data in Table 2 indicates that of the various antioxidant packages, Samples 5 and 6, containing the synergistic acridan compound of this invention, provide equivalent or better performance than the commercial packages evaluated.

DSC ANALYSIS OF POLYOL

Differential scanning calorimetry (DSC) measures the endothermic or exothermic heat of reaction and can give the precise temperature of this initial reaction. A sample weight of approximately 30 mg was placed in the sample chamber of a Perkin-Elmer DSC-2C. The instrument was equlibrated, under nitrogen flow, to 130°C. Once equilibrated, the gas in the sample chamber was switched from nitrogen to air at a flow rate of 100 cc/min and the temperature ramped at 10°C/min with the temperature in K recorded at the time of the exotherm. The DSC results shown in Table 2 shows samples 5 and 6, containing the synergist of this invention, to be superior to all other packages evaluated.

Additionally, APHA color testing of the polyols stabilized with samples 1-6, as well as an unstabilized polyol sample, are presented in Table 2. The APHA Platinum-Cobalt system used follows ASTM D1209. The values on this scale range from 0 (water white) to 300 (cream white). This data is presented because of the importance of color to the polyol manufacturers. The lower values, indicating lightest color, are those most desirable.

It can be seen from the data that the addition of any stabilizer package adds to the APHA, but the value of sample 2, with stabilizer package containing the synergistic compound of this invention, is equal to the lowest value for a commercially available stabilizer package.

TABLE 2

Example #	DSC (K)	APHA color	TGA analysis:weight loss(°C) initial	10%	20%
A	496.1	30	202	230	230
B	503.0	35	215	236	242
C	492.9	25	203	224	233
D	503.3	30	211	227	236
1	505.4	30	212	238	244
2	504.2	25	212	236	243

The aforementioned polyether polyols are used in the production of slabstock flexible polyurethane foam. Samples of polyurethane foam were made and tested by thermogravimetric analysis and microwave scorch as well.

Testing conditions used to evaluate polyurethane foam samples were the same as conditions used in the evaluation of polyol by TGA (described above) except that the sample weight was approximately 8 mg because of the increased density of the foam. Platinum wires were used to compress the foam samples onto the aluminum sample pan in order to obtain a reasonable sample weight.

The small hand-mixed foam samples were made by the procedure below, and is typical of formulations used by the polyol manufacturers. A premix of 10.0 grams of water, 0.30 grams of an amine catalyst (Dabco 33-LV sold and trademarked by Air Products & Chemicals) and 2.0 grams of a surfactant (L-5810, a tin catalyst sold by Union Carbide) was added to 200 grams of a 3000 average molecular weight polyether polyol which had minimal initial stabilization (100 ppm BHT) but also containing the stabilizer package indicated in Table 1. The formulation may also contain a flame retardant as used by foam manufacturers. These flame retardants are typically chlorinated, chlorinated and brominated or brominated phosphates. The mixture was stirred for five seconds in a high speed Lightning Mixer. Then 0.40 grams of tin catalyst (stannous octoate in dioctylphthalate) was added and the resulting mixture stirred for five seconds in the Lightning Mixer. Finally, 126.0 grams of toluene diisocyante (TDI-80, 80% 2,6-/20% 2,4-toluene diisocyante sold by Mobay) was added and the mixture stirred in the Lightning Mixer for 7 seconds and subsequently poured into a 10" x 10" x 5" cardboard box. The foam was allowed to rise completely at room temperature.

These foams were not subjected to any additional heating either by microwave or air circulating oven.

The foam buns were allowed to stand for a day, with samples taken midway between the center and the outer surface of the foam bun. Table 3 shows the performance of the commercially available as well as the experimental stabilizer packages that are the subject of this invention. Examples 1 and 2 demonstrate superior performance as compared to comparative Examples A-D.

The microwave scorch test is a rapid and reproducible small scale test which correlates well with observed results from large machine prepared foams. This procedure utilizes small hand mixed foam samples in order to evaluate the effectiveness of antioxidant packages. Because foam buns will dissipate the internal heat more rapidly than foam buns produced on an industrial scale, a microwave oven is used to uniformly heat the foam bun by radiant energy rather than by conduction of heat. This promotes uniform heating of the small foam bun resulting in reproducible scorch values. The formulation used to prepare the foam buns is given above, and is typical of the formulations used in the industry.

After the formulation was prepared, it was poured into a 10" x 10" x 5" cardboard box and allowed to rise. Five minutes after the appearance of bubbles on the surface of the foam, the sides of the box are pulled away from the foam bun and immediately placed into a preconditioned microwave oven for 5 minutes and 30 seconds at 60% power. The microwave oven is preconditioned by heating a 1000 ml beaker containing 600 ml of water for 30 minutes prior to the first foam bun tested, with a fresh beaker returned to the microwave for each bun tested, to maintain a constant temperature and humidity within the microwave during testing.

Upon removal of the foam bun from the microwave oven, it is placed into an air circulating oven for 3 minutes at 125°C to cure the skin of the bun. Upon removal from the air circulating oven, the foam sample was cut in half, perpendicular to the rise of the foam and inspected for degree of scorch. A one-inch thick slice is cut from the center of each bun and analyzed via a Hunter Lab Colorimeter, Model D25M/L.

The Hunter Color values on both the B scale (measuring yellowness or blueness) and the E scale (total color difference compared to white) were compiled for all six samples and may be found in Table 3. These data demonstrate that comparative Example D provides the highest scorch protection of the commercial systems evaluated, while Example 1 provides a slight increase in scorch protection over the Example C, while Example 2 provides a sizeable increase in scorch protection over comparative Example D.

TABLE 3

Example #	TGA:%WT Loss		Microwave Scorch	
	190°C	250°C	Hunter B	Hunter E
A	99.3	88.3	21	38
B	99.3	89.0	22	37
C	99.3	88.0	19	32
D	99.3	88.5	11	15
1	99.4	89.3	18	25
2	99.4	89.5	6	10

STABILIZATION OF OTHER POLYMERIC SYSTEMS

The acridans of the invention may be used in a wide variety of polymers and long chain hydrocarbons which do not contain sulfur linkages in the chains. These may include polyolefins, petroleum based oils, lubes and greases as well as polyalkylene glycols, preferably polyethylene glycols and methoxy polyethylene glycols such as the Carbowax family of products (trademarked and marketed by Union Carbide Chemical and Plastics Company). These oxidizable compositions benefit greatly from use of the stabilizer systems described herein.

Various stabilization systems, including several containing the acridan synergists of this invention, were evaluated in polyglycol. The polyglycol used was P-2000 (a product of Dow Chemical) and the stabilizers employed included the comparative control, BHT, described above.

COMPARATIVE EXAMPLE E AND EXAMPLES 3-5

To a 10 gram commercial sample of P-2000 polyglycol, 1.0% of each stabilizer package was added. The samples were evaluated via differential scanning calorimetry as described above using a Perkin-Elmer DSC Model 2C which was calibrated using an indium standard. Approximately 7 mg of samples were weighed into an aluminum pan and were equilibrated at 373 K with nitrogen flow, and then ramped at 10° K/min with air flow of 50 cc/min until exotherm. The content of each stabilizer package along with the temperature to exotherm, is presented in Table 4 below.

TABLE 4

Example #	E	3	4	5	6
Component					
Naugard 445	-	0.5	0.5	0.5	1.0
BHT	1.0	-	-	-	
AC1	-	0.5	-	-	
AC2	-	-	0.5		
AC3	-	-	-	0.5	
Temp to Exotherm (C)	198	256	253	247	215

The above DSC results show a consistently higher temperature to exotherm. The Acridans of the invention, AC1, AC2, AND AC3 show markedly higher temperatures to exotherm than the recognized control BHT, or when

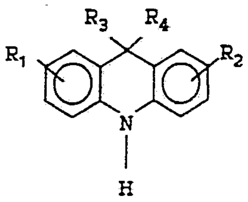
Naugard 445 is run by itself.

The data presented herein are intended to illustrate, but in no way to limit the scope of the invention. Other variations will be evident to those skilled in the art and such modifications are intended to be within the scope of this invention as defined by the following claims.

What is claimed is:

1. A sulfur-free oxidizable composition stabilized against thermal and oxidative degradation by the incorporation therein of a minority amount of a stabilizer system comprising:

at least one acridan compound of the structure:

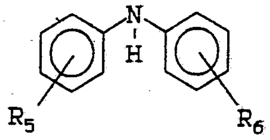


I

wherein R_1, R_2, R_3, R_4 can be H, C_1-C_{18} alkyl or C_7-C_{18} aralkyl and R_3 and R_4 may be aryl.

2. The oxidizable composition of claim 1 further comprising:

an amine stabilizer of the structure

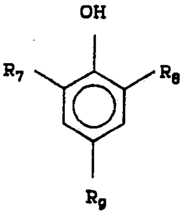


II

wherein R_5 and R_6 are individually selected from H, C_1-C_{18} alkyl, C_7-C_{18} aralkyl.

3. The oxidizable composition of claim 1 further comprising:

a phenolic stabilizer of the formula



III

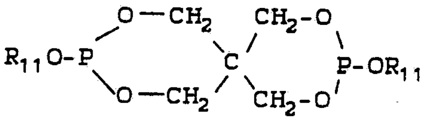
wherein R_9 can be C_1-C_{18} alkyl or C_7-C_{18} aralkyl and R_7 and R_8 are C_4-C_{18}, C_7-C_{12} aralkyl.

4. The oxidizable composition of claim 1 further comprising:

a phosphite stabilizer of the formulas

$(R_{10}O)_3$-P

IV



V

wherein R_{10} and R_{11} are independently selected from

C_6-C_{18} alkyl, aryl, C_7-C_{18} aralkyl, or C_7-C_{18} alkaryl.

5. The oxidizable composition of claim 1 wherein R_1 and R_2 are hydrogen and R_3 and R_4 are alkyl.

6. The oxidizable composition of claim 1 wherein R_1 and R_2 as hydrogen and R_3 and R_4 as methyl.

7. The oxidizable composition of claim 2 wherein R_5 and R_6 are alpha,alpha-dimethylbenzyl.

8. The oxidizable composition of claim 3 wherein R_9 is sec-butyl or methyl and R_7 and R_8 are t-butyl.

9. The oxidizable composition of claim 1 wherein a majority of said composition is a polyoxyalkylene polyether polyol.

10. The oxidizable composition according to claim 9 wherein the acridan is present in the amount ranging from about 1 to about 10% by weight.

11. The oxidizable composition of claim 1 wherein said acridan is present in from about 0.1 to about 2.0 weight percent with the remainder of said oxidizable composition being polyglycols, heat transfer fluids, and hydrocarbon oils, greases or lubricants.

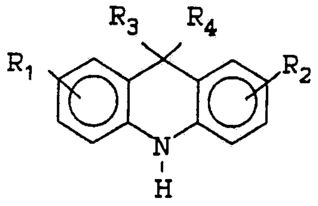
12. The manufacture of flexible polyurethane slabstock manufactured from an isocyanate and polyether polyols stabilized by the stabilizer system of claim 1.

13. A polyether polyol composition stabilized against degradation comprising:

(a) a polyether polyol and;

(b) a stabilizer system comprising:

1) at least one acridan compound of the structure:



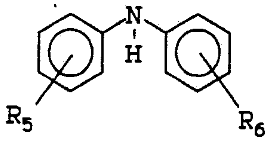
I

wherein R_1, R_2, R_3, R_4 can be H, C_1-C_{18} alkyl or C_7-C_{18} aralkyl and R_3 and R_4 may be aryl and;

(2) at least one additional compound selected from the group consisting of highly hindered amine, phenolic or phosphite compounds known to exhibit stabilizing properties.

14. The oxidizable composition of claim 1 wherein said additional compound comprises:

an amine stabilizer of the structure

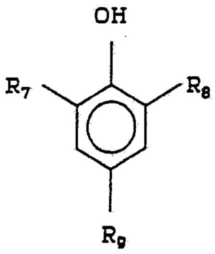


II

wherein R_5 and R_6 are individually selected from H, C_1-C_{18} alkyl, C_7-C_{18} aralkyl, or C_7-C_{18} alkaryl.

15. The composition of claim 1 wherein said additional compound comprises:

a phenolic stabilizer of the formula



III

wherein R_9 can be C_1-C_{18} alkyl, C_7-C_{18} aralkyl, or and R_7 and R_8 are C_4-C_{18} alkyl, C_7-C_{12} alkyl.

16. The polyether polyol composition of claim 1 wherein said additional compound comprises:

a phosphite stabilizer of the formula IV

$$(R_{10}O)_3\text{-}P$$

IV

17. A composition according to claim 1 further comprising a phenothiazine.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/07227

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08K5/3437; C10M133/40; C09K15/30

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08K

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	US,A,3 406 144 (B.A. MARSHALL) 15 October 1968 see abstract; claims see column 3, line 7 - line 70 ---	1-4, 14-16
X	US,A,4 794 126 (G. FESMAN ET AL.) 27 December 1988 cited in the application see abstract; claims see example ---	1,9-13
X	US,A,3 003 995 (E.C. SCHULE) 10 October 1961 see claims see column 2, line 36 - line 65 ---	1,2,14
	-/--	

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1 **IV. CERTIFICATION**

Date of the Actual Completion of the International Search 29 OCTOBER 1992	Date of Mailing of this International Search Report -5. 11. 92
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer METTLER R.M.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	EP,A,0 223 000 (ALLIED CORPORATION) 27 May 1987 see page 3, line 23 - page 4, line 34 see page 7, line 35 - page 8, line 29 see page 11; example 4 ---	1,11
A	DE,B,1 163 829 (GEIGY AG) 27 February 1964 see column 1, line 5 - column 2, line 49 see claim -----	1,11,12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/07227

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

./.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

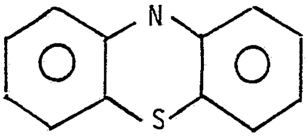
☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/

Claims searched completely 1 - 16
Claims not searched 17

Contradictions

Claim 1: Sulfur-free composition
Claim 17: Composition of claim 1 further comprising phenothiazine



ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9207227
SA 64166

29/10/92

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		GB-A-	1005371	
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		NL-A-	272329	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82