United States Patent Office

3,029,257
Patented Apr. 10, 1962

3,029,257

STABILIZED SATURATED CYCLIC ETHER COMPOSITIONS

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No Drawing. Filed Nov. 20, 1959, Ser. No. 854,236
2 Claims. (Cl. 260—346.1)

This invention relates to the stabilization of cyclic ethers, particularly saturated ethers and more particularly to the stabilization of tetrahydrofuran.

Tetrahydrofuran and related compounds are susceptible to oxidation and have a tendency to form peroxides Peroxides are especially undesirable because if permitted to increase to high concentrations, the material can become too unsafe for handling. Peroxides usually form under storage conditions when the ether is in contact with air. Additional peroxide formation can occur when the ether is used and exposed to light and air. In order to prevent the peroxide from exceeding safe limits, it is necessary to employ stabilizers or antioxidants that either destroy the peroxide, inhibit its formation, or both.

A preferred stabilizer in addition to effectively suppressing peroxide formation or accumulation is one that is non-toxic and substantially colorless. Additionally, the stabilizer should be effective when used at low concentrations. Known antioxidants are frequently unsuitable either because they do not suppress peroxide formation or accumulation to a sufficiently low level or because they do not possess the above characteristics.

It has been found that excellent stabilization can be obtained using 4,4'-thiobis-(6-tertiary-butyl-m-cresol). The above-disclosed stabilizer is essentially nontoxic and tetrahydrofuran and related compounds stabilized according to the present invention remain substantially colorless under the influence of air and light.

It is an object of the present invention to provide a stabilized cyclic ether composition that does not develop excessive peroxide formation.

It is another object of the present invention to provide a stable tetrahydrofuran composition that does not become discolored under the influence of light and air.

It is still another object to provide a method of effectively stabilizing tetrahydrofuran and related ethers against peroxide formation.

These and other objects will be apparent from the following examples and description.

Concentrations of less than 0.01 to more than 1% by weight of 4,4'-thiobis-(6-tertiary-butyl-m-cresol) are effective in preventing peroxide formation in saturated cyclic ethers and related compounds. More than 1% by weight can be used but preferred concentrations are those having 0.01 to 0.1% by weight of the stabilizer.

Two 250 ml. Erlenmeyer flasks were equipped with cork stoppers fitted with tubing which permitted the entrance of air. A 100 ml. sample of tetrahydrofuran was placed in each flask and about 0.1 gm. of 4,4'-thiobis-(6-tertiary-butyl-m-cresol) was introduced into one sample. The tetrahydrofuran used had a very low peroxide content when received (less than 50 p.p.m.). The flask was constantly exposed to light and air for an extended period of time at room temperature and tetrahydrofuran peroxide content (p.p.m.) was determined periodically as follows:

Days of Exposure	Tetrahydrofuran Peroxide (p.p.m.)	
	Stabilized	Unstabilized
7	70	2,200
14	115	2,800
21	345	9,900
35	115	19,150
49	90	Discontinued
105	240	Discontinued

From the above it can be seen that the 4,4'-thiobis-(6-tertiary-butyl-m-cresol) stabilizer had an extraordinary effect in preventing peroxide formation. In addition to containing a non-toxic stabilizer, the stabilized composition remained colorless throughout the experiment.

Other cyclic ethers which can be stabilized in accordance with the present invention include methyl tetrahydrofuran and tetrahydropyran.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A stabilized composition consisting essentially of a saturated cyclic ether selected from the group consisting of tetrahydrofuran, methyl tetrahydrofuran, and tetrahydropyran and from 0.01 to 1% by weight 4,4'-thiobis-(6-tertiary-butyl-m-cresol).

2. A stabilized composition consisting essentially of tetrahydrofuran and about 0.01 to 0.1% by weight 4,4'-thiobis-(6-tertiary-butyl-m-cresol).

References Cited in the file of this patent

Thompson et al.: Ind. and Eng. Chem., vol. 42, pages 922–925 (1950).

Katsui et al.: Chem. Abstracts, vol. 51 (1957), columns 15, 887–8.