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DISTILLATION OF ETHERS CONTAINING PEROXIDES

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The present invention relates to a method of preventing explosions upon heating certain oxygen-containing liquids which normally tend to develop peroxides during storage which comprises distilling said peroxide-containing liquids in the presence of small amounts of solvent oil of petroleum origin.

Several reports have been published telling about explosions which have occurred when isopropyl ether, which had been known to have been stored for a substantial length of time (5 years in one case), was subjected to distillation; the explosion occurred toward the end of the distillation. The theories advanced to explain these explosions suggest that, upon storage, isopropyl ether is converted into a peroxide and it is this peroxide which, when subjected to heat, in a relatively high concentration (as in the case when most of the isopropyl ether has been distilled off), undergoes decomposition with explosive violence.

It is a primary object of the present invention to stabilize isopropyl ether and similar compounds so as to prevent their explosion on distillation whether or not they contain very much peroxide, because usually unless the material is subjected to careful analysis the prospective user will not know whether the ether contains much peroxide or not. This and other objects of the invention will be apparent to those skilled in the art from a reading of the following description.

It has been discovered that the explosion of isopropyl ether containing a small amount of peroxide can be prevented by adding to the ether a small amount of a high-boiling hydrocarbon oil as a stabilizer. Probably the stabilization is the result of two factors: (1) having a small amount of rather high-boiling liquid present which will prevent the distillation flask or other container from becoming highly overheated after the bulk of the isopropyl ether has been distilled off, and (2) the presence of the high-boiling oil even though relatively small in quantity compared to the amount of ether originally present serves as a diluent to prevent the peroxides from being present in too great a concentration.

The following is an example of the operation of the invention:

Upon evaporation of 25 ccs. of an old sample of isopropyl ether in an evaporating dish on an electric hot plate, the residue decomposed with an audible explosion. However, when the same test was repeated with a sample of the same isopropyl ether to which 1% of a stabilizer had been added, no decomposition of the residue occurred. The stabilizer used in this instance was a hydrocarbon oil of a very light lube oil boiling range and obtained from a naphthenic base crude petroleum. This sample of oil had the following approximate inspection characteristics:

Gravity	°A. P. I.	25.6–26.3
Flash point	°F.	300–320
Viscosity at 100° F. (secs. Saybolt Univ.)		75–85
Pour point	°F.	15 to −30
Aniline point	°F.	158–165

When a hydrocarbon oil is used as stabilizer, preferably it should have physical characteristics falling within the following ranges:

Gravity, °A. P. I.	18–28, 50% B. pt. above 350° F. at 10 mm.
Flash	270–375° F.
Visc. Saybolt at 100° F.	70–450 secs.
V. I.	Preferably not more than 50

It should be understood, of course, that other hydrocarbon oils having a mid-boiling point of at least 400° F. and preferably at least 500° F. at atmospheric pressure, may be used, although the oils having the above listed characteristics are preferred. These oils may be prepared either by distillation of selected crudes, preferably naphthenic or asphaltic base crudes, or may be obtained by solvent extraction of various crudes with selective solvents such as sulfur dioxide, phenol, etc. having a selective solvent action for aromatic hydrocarbons. The oils to be used should be relatively free from unsaturated aliphatic compounds. Other fractions of hydrocarbon oils can be used, for instance, kerosene, mineral seal oil, straw oil, pale lube oil, etc.

Other types of liquid organic mixtures or compounds can be used as stabilizers, even oxygen-containing compounds, providing they do not normally tend to develop peroxides themselves upon storage. For example, diphenyl oxide and other similar high-boiling compounds or chlorinated derivatives such as chlorinated diphenyl, may be used.

The amount of the stabilizer to be used may be approximately from 0.1 to 5.0% or so, depending upon the expected time of storage or the relative severity of the storage conditions, as far as peroxide-forming tendencies are concerned. For example, for storing an ether in the dark at low temperature and for a short time, only a relatively small amount of stabilizer would be sufficient, whereas for storing in the presence of light, espe-

cially strong light such as sunlight or ultraviolet light, and at elevated temperature in the presence of oxygen and over a long period of time, a large amount of stabilizer should be used.

Although the invention has been illustrated with isopropyl ether particularly, it may also be applied to other ethers such as methyl isopropyl ether, isopropyl tertiary butyl ether, and other ethers containing a branched aliphatic group attached to the ether-oxygen atom or to other ethers containing aliphatic groups such as diethyl ether or even mixed aliphatic aromatic ethers such as ethyl phenyl ether or isopropyl phenyl ether. The invention is believed particularly advantageous with ethers having the general formula ROR' in which at least one of R and R' is a branched aliphatic hydrocarbon radical and both R and R' are hydrocarbon groups.

Apparently, the tendency of the ethers to form peroxides is substantially accelerated by small amounts of materials which tend to catalyze the reaction such as acetaldehyde or other aldehydes or perhaps even other types of compounds such as acetic acid. Since the formation of peroxides is substantially due to a chemical combination of oxygen in the ether molecule, it is desirable to also add a small amount of oxidation inhibitor to the ether, for instance, alpha naphthol, benzyl para-amino phenol, or other aromatic hydroxy and amino compounds or derivatives thereof which serve as oxidation inhibitors. The amount of such inhibitors is generally between 0.01 and 1.0%, preferably from 0.02 to 0.2% on the basis of the weight of the ether. However, even though the presence of such an oxidation inhibitor tends to prevent or reduce the formation of peroxides in the ether, yet it is desirable to have some of the stabilizer proposed herewith also present as a precaution so that if the amount of the oxidation inhibitor was not sufficient to forestall the formation of peroxides or if the time of storage was substantially longer than the time during which the oxidation inhibitor can safely carry out its inhibiting functions, and peroxides are thus actually formed, still an explosion would be prevented due to the presence of the stabilizer.

The use of the present invention, for example, by the addition of a small amount of pale lubricating oil to isopropyl ether, does not prevent such ethers from being used for most of the purposes for which they had previously found use, for instance, as solvent (e. g. for resins, waxes, fats, oils, fatty acids, etc.) or as anti-knock addition agents for motor fuels (according to the Buc Patent 2,046,243).

Although the manufacture of the ethers such as isopropyl ether is not part of this invention, it is noted that the Rosen et al. Patent 2,105,508 discloses a suitable method for manufacturing isopropyl ether. The stabilizer proposed according to the present invention in preferably added to the ether as soon as possible during the process of finishing the ether.

It is not intended that this invention be limited to any of the specific examples given above for illustration only, nor to any theories of the operation of the invention, but only by the appended claims in which it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

I claim:

1. A process which comprises adding to a peroxide-containing alkyl ether a small amount of a petroleum oil fraction boiling between about kerosene and about light lubricating boiling ranges and distilling the same.

2. a process which comprises adding to a composition comprising essentially a peroxide-containing ether a small amount of a petroleum oil fraction boiling between about kerosene and about light lubricating oil boiling ranges and distilling the same.

3. A process which comprises adding to a peroxide-containing ether a petroleum oil fraction of naphthenic origin in amounts between about 0.1% and about 5% and distilling the resulting composition.

4. In a process of preventing explosions in the purification of iso-alkyl ethers which normally tend to develop and contain peroxides, the step of distilling such ethers in the presence of a small amount of a petroleum oil fraction boiling between about kerosene and about light lubricating oil boiling ranges.

5. A process as in claim 4 wherein the petroleum oil fraction added was obtained from a naphthenic base crude and was added in an amount between about 0.1% and about 5%.

6. A process which comprises adding to isopropyl ether containing peroxides formed by the partial oxidation of said iso-propyl ether a small amount of a petroleum oil fraction having an A. P. I. gravity between about 18 and about 28, a flash point between about 270° F. and about 375° F., a Saybolt viscosity at 100° F. of between about 70 and about 450 seconds, and a viscosity index less than 50, and distilling the resulting composition.

7. The process as in claim 6 wherein the petroleum oil fraction is added in an amount between about 0.1 and about 5%.

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