Stabilization of Isopropyl Ether

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ETHERS AND ether-like compounds are known to undergo autoxidation during conditions encountered in normal storage at ambient temperature. Peroxides are formed which, in the case of ethers that may be distilled or vaporized at temperatures lower than the decomposition temperatures of the peroxides, may build up to dangerous concentrations. Of the numerous ether substances which are subject to autoxidation, isopropyl ether is extremely susceptible to this type of deterioration with the formation of a high boiling, dangerously explosive peroxide.

Instances have been reported in this laboratory of minor explosions of this ether occurring toward the end of standard distillations conducted during specifications analyses. More serious and violent explosions have also occurred when larger volumes of this ether which were not freshly distilled were utilized in the laboratory for extraction and other uses. Warnings of explosions of isopropyl ether handled in the above manner due to the presence of peroxides have also been issued by other laboratories (*8, 14*).

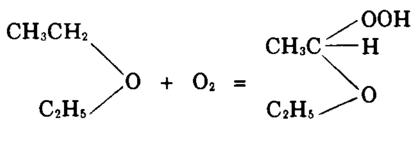
While various means have been proposed for removing peroxides from ethers, such as treatment with sodium hydroxide solution followed by steam distillation, agitation with ferrous sulfate solution, or addition of mercury or permanganate, these methods are time-consuming and costly, and may introduce impurities in the ether.

Very small amounts of certain chemicals are frequently added to refined products to inhibit deterioration during storage. Many substances which prevent autoxidation of ethers have been tested and described (*6*). Phenol, polyphenols, diphenylamine, and aromatic amines were found to be effective stabilizers for anesthetic ether (*11*). A number of patents on stabilization of ethers, based upon incorporation of small amounts of chemicals, have been issued (*4, 5*). Attempts were therefore made to stabilize isopropyl ether against peroxide formation for long periods of time by the addition of small amounts of substances which would not affect its purity, rather than undertake removal of the peroxides before subsequent use of ether that had not been freshly distilled.

THEORIES OF AUTOXIDATION AND INHIBITION OF PEROXIDATION OF ETHERS

The fundamental mechanism of the autoxidation of ethers has been the subject of numerous investigations. Many different views have been advanced concerning the chemistry involved. Brief mention is made here of only a few of these theories. Those who wish to pursue further studies on this aspect of the deterioration of ethers should refer to a recent review and excellent summary of the various theories on oxidative processes by Reiche (*9*).

Clover (*3*) studied the spontaneous decomposition products and the action of dilute acid on the ether peroxide and concluded that the peroxide is formed simply by displacement of one hydrogen atom on one of the methylene groups by a molecule of oxygen as follows:

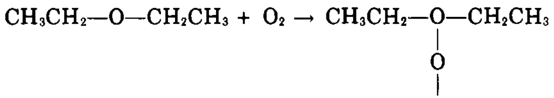


Milas (*7*) reported that Wieland and Wingler disagreed with the view of Clover and postulated that the autoxidation process begins with dehydration of the ether to vinyl ethers with formation of hydrogen peroxide. The vinyl ethers then hydrolyze to form ethyl alcohol and acetaldehyde.

$$CH_3CH_2{-}O{-}CH_2CH_3 + O_2 \rightarrow CH_3CH_2{-}O{-}CH{=}CH_2 + H_2O_2 \qquad (1)$$

$$CH_3CH_2{-}O{-}CH{=}CH_2 + H_2O \rightarrow CH_3CH_2{-}O{-}CHOHCH_3 \rightarrow CH_3CH_2OH + CH_3CHO \qquad (2)$$

Milas (*7*) himself proposed a theory to account for the mechanism of autoxidation of various compounds. Applied to ethers his view is that autoxidation proceeds by the primary addition of molecular oxygen to the bivalent oxygen atom of the ether in the following manner:



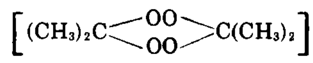
$$CH_3CH_2{-}O{-}CH_2CH_3 + O_2 \rightarrow CH_3CH_2{-}\underset{\substack{|\\ O\\ |\\ O}}{O}{-}CH_2CH_3$$

Present knowledge concerning the chemistry involved in the autoxidation of ethers is included in this publication. Reiche reports that one of the autoxidation products of isopropyl ether was found to be dimeric acetone peroxide and advanced the view that two molecules of oxygen react with the ether to form bis(hydroperoxy-isopropyl) ether as the first oxidation product.

$$(CH_3)_2CH{-}O{-}CH(CH_3)_2 + 2O_2 \rightarrow (CH_3)_2COOH{-}O{-}COOH(CH_3)_2$$

Bis(hydroperoxy-isopropyl) ether

The hydroperoxide by splitting out water may then decompose into peroxidic fragments which, by combination, yield dimeric acetone peroxide



While many different views have been advanced concerning the exact mode of autoxidation of ethers, there is agreement on some of the more practical aspects of the autoxidation process, such as deterioration by reaction with oxygen to form peroxides. The peroxides, by interaction or decomposition, or both, yield aldehydes, acids, and other deleterious impurities. It is known that deterioration of the ethers increases with time and is favored by the presence of oxygen. Exposure to light and heat accelerates the rate of autoxidation. Contact with contaminating metals may promote peroxide formation in ether.

The action of antioxidants in retarding the peroxidation of ethers may be explained on the basis that autoxidation "is a chain reaction with very long reaction chains" (*10*), and that antioxidants added to the ether break the chain reactions (*1*) in the system or act as chain-terminating agents. Amines, however, may function in a different manner than antioxidants as peroxide inhibitors. Capp and Hawkins (*2*) found that hydroperoxides may be readily decomposed in the presence of a variety of amines, and

Whitby and others (*13*) experimented with amines as activators for decomposition of peroxides in polymerization processes and found that many are capable of decomposing organic peroxides. The effect of amines as stabilizers for ethers may therefore be that of peroxide destruction rather than inhibition of the autoxidation chain reaction.

EXPERIMENTAL

Storage Containers. In early exploratory tests it was found that the rate of peroxidation of isopropyl ether in storage was dependent upon the type of container used. In all cases the rate of autoxidation was most rapid when the ether was stored in clear glass bottles. In order to test the effect of the peroxide inhibitors under conditions in which the ether would be most susceptible to autoxidation, clear glass containers were chosen for most of the tests. In some of the tests, 1-quart and 5-pint clear, glass, glass-stoppered bottles were used. Gallon-size, clear glass, screw-top bottles were used in another series of tests. Bulk storage of the ether was conducted in 5-gallon iron containers. Storage of unhibited ether was also conducted in a 5-gallon iron container and in an iron container coated with a baked phenolic-type resin, primarily to test the possible effect of iron as a peroxide inhibitor and to determine the effect of the coating on preserving the purity of the product.

Isopropyl Ether. The ether used for all of the stability tests was freshly distilled, commercial material (Union Carbide Chemicals Co.). Typical analyses were:

Specific gravity 20/20° C.	0.7250
Distillation at 760 mm.	
Initial Boiling Point	66.6° C.
Dry Point	68.8° C.
Propionic acid, %	Trace
Water	Dry to anhydrous copper sulfate
Meq. oxygen/gram ether	None
Color, Pt-Co standard	3
Suspended matter	Small amount present
Odor	Satisfactory

Procedure. Quart and 5-pint clear glass bottles which had previously been cleaned with strong chromic acid solution, rinsed, and dried, were filled with freshly distilled isopropyl ether. The calculated amount of inhibitor was added and the containers were set aside on the laboratory shelf at room temperature, unshielded from daylight. A control sample of ether, to which no inhibitor was added, was set aside under the same storage conditions.

In the 5-gallon drum storage tests, the calculated amount of inhibitor for the ether was first added to the container. The drums were then filled. Two drums, one iron and one resin-coated, were filled with ether containing no inhibitor and reserved as controls. One gallon of ether from each of the drums was subsequently transferred to 1-gallon, clear glass, screw-top bottles for comparative stability tests.

The amines used in the tests were refined grade materials and were added directly to the ether. *N*-Benzyl-*p*-aminophenol cannot be added directly to the ether because an insoluble constituent of this product separates and contaminates the ether. The recommended procedure for adding this inhibitor is to prepare a saturated solution of the antioxidant in isopropyl ether. The insoluble portion may be removed by filtration and the filtrate then reserved as a stock solution for inhibiting the refined ether.

Analyses. The specification analyses as illustrated above were made on the ether at the start and end of the test. These analyses were omitted, however, at the end of the tests in the case of the control samples which had autoxidized to the extent that standard distillation would have been hazardous.

The progress of ether autoxidation was followed at intervals throughout the storage period by determination of the ether peroxide content. The peroxide was determined by addition of postassium iodide to the ether solution just previously acidified with sulfuric acid solution, and titration of the liberated iodine with sodium thiosulfate.

DISCUSSION AND RESULTS

Some noteworthy observations were made during the initial investigation concerning peroxidation of the ether. Peroxidation of the ether was accelerated by the presence of oxygen from the air and by heat. Alkalies, ammonia, and some of the ethanolamines had a retarding effect on autoxidation. Light had an accelerating effect, as shown by relative peroxidation rates of ether stored in clear and amber-colored bottles. Storage of ether over sodium hydroxide solution or water retarded peroxidation, and peroxides already present in the ether could be effectively removed by shaking with the alkaline solution. Concentrated solutions containing approximately 20 to 30 meq. of oxygen per gram of ether were prepared in small quantity from isopropyl ether. The peroxide readily liberated iodine from potassium iodide, had a strong acid odor, and was highly explosive when heated.

In the early studies undertaken, numerous insoluble inhibitors were tried, none of which could be relied upon to retard autoxidation of the ether. One of the *N*-substituted *p*-aminophenols, *N*-benzyl-*p*-aminophenol, described by Rogers (*12*) as an effective antioxidant for freshly cracked gasoline, was the first successful stablizer found. This compound was used with excellent results for stablization of all isopropyl ether produced in the plant until the availability of the antioxidant was curtailed during World War II. A search was then made for substitute stabilizers for isopropyl ether.

The data of Table I are included to show the relative effect of several of the gasoline antioxidants on the peroxidation of isopropyl ether and to furnish a basis of comparison for the substitute stabilizers investigated later. In this test the ether was stored at room temperature, unshielded from daylight in 5-pint, clear glass, glass-stoppered bottles. *N*-Benzyl-*p*-aminophenol in a concentration of 16 p.p.m. preserved the solution entirely free from peroxides for 90 weeks. Autoxidation proceeded rapidly in the case of the ether to which no antioxidant was added. Addition of the antioxidants to the ether to the extent of 16 p.p.m. had no harmful effects on the purity, as determined by specification tests.

A number of alkanolamines and alkylamines were screened as possible substitutes for the *N*-benzyl-*p*-aminophenol. All of the amines were added in a concentration of 0.04% by weight in the ether. While autoxidation was effectively retarded by most of the amines, some had a deleterious effect on the purity of the ether at the concentration level used. In general, the alkylamines were more effective as antioxidants than the alkanolamines. The screening tests were conducted in 1-quart, clear glass, glass-

Table I. Effect of Gasoline Antioxidants on Autoxidation of Isopropyl Ether

Antioxidant	Concn. P.P.M.	Storage Period, Weeks 4	8	90
		Meq. Oxygen/G. Ether		
None (control)	...	0.389	0.565	6.09[b]
N-alkyl aminophenol[a]	16	0.001	0.001	0.007
N-isobutyl-*p*-aminophenol	16	0.003	0.001	0.006
N-benzyl-*p*-aminophenol	4	0.001	Nil	2.03
	12	0.001	Nil	0.006
	16	0.003	Nil	Nil
	32	0.001	Nil	0.001

[a] E.I. du Pont de Nemours & Co., Inc.

[b] Meq. oxygen/gram ether 9.2 after 4 years of storage.

Table II. Effect of Amines on Autoxidation of Isopropyl Ether

Alkanolamine	Concn., % by Wt.	Storage Meq. Oxygen/G. Ether 1 month	 21 months
None control	...	0.301	5.08
Monisopropanolamine	0.04	0.041	0.247
Diethanolamine	0.04	Nil	0.627
Diisopropanolamine	0.04	0.004	1.42
Triisopropanolamine	0.04	0.004	0.19
Phenylethanolamine	0.04	Nil	0.18
Alkylamine			
Diphenylamine	0.01	0.001	0.042
Morpholine	0.04	Nil	0.015
Ethylenediamine	0.04	Nil	0.009
Diethylenetriamine	0.04[a]	Nil	0.003
Triethylenetetramine	0.04[a]	Nil	Nil
Tetraethylenepentamine	0.04[a]	Nil	Nil

[a] Ether became slightly turbid when amines were first added but soon clarified.

stoppered bottles unshielded from daylight. The peroxide content of the ether after 1 month and again after 21 months of storage is given in Table II.

In some instances a very slight turbidity of the ether occurred upon addition of some of the ethylene amines. The turbidity was a temporary phenomenon only, and after a few hours the ether samples clarified and thereafter passed all specification tests previously described for purity.

The optimum amount of amine required for preservation of the ether will, of course, depend on the amine used and the storage conditions.

The data of Table III were obtained from storage of the ether in 1-quart, clear glass, glass-stoppered bottles unshielded from daylight. The data indicate that 100 to 400 p.p.m. of morpholine in the ether would be sufficient to preserve the ether virtually free from peroxide for prolonged storage periods even under the most adverse conditions. Very low concentrations of the other alkylamines (10 to 50 p.p.m.) were sufficient to prevent autoxidation of the ether. When quantities of these ethylene amines much greater than 50 p.p.m. were added to the isopropyl ether, a slight amount of brown, viscous material sometimes settled out on the bottom or sides of the container. This small amount of material adhered tenaciously to the container, but did not affect the quality of the ether in any manner.

Table III. Optimum Concentration of Alkylamines Required

Compound	Concentration of Amine in Ether, Wt. % 0.001	 0.005	 0.010	 0.040
	Meq. Oxygen/G. Ether after 6-Month Storage			
Morpholine	0.017	0.044	0.007	0.001
Ethylenediamine	0.019	0.003	0.007	0.002
Diethylenetriamine	0.004	0.001	0.001[a]	0.002
Triethylenetetramine	0.001	0.003	0.001[a]	Nil
Tetraethylenepentamine	0.009	0.001	0.002	0.002

Peroxide content in three control samples was 0.55, 0.68, and 0.90 meq. of oxygen per gram of ether.

[a] Very slight amount of brown viscous material on bottom of test container.

The relative effect of the ethylene amines was compared directly to the effect of N-benzyl-p-aminophenol as antioxidants under identical storage conditions for a prolonged period of time, 1370 days in 5-gallon iron containers and 520 days in 1-gallon, clear glass containers. The results are summarized in Table IV.

Morpholine and ethylenediamine at the concentrations shown were somewhat less effective than N-benzyl-p-aminophenol during prolonged storage in both iron and glass containers, while the other ethylene amines tested were as effective antioxidants as the N-benzyl-p-aminophenol.

Table IV. Comparative Effect of N-Benzyl-p-Aminopheno and Alkylamines on Autoxidation of Isopropyl Ether

Amine	Concn., p.p.m.	Meq. Oxygen/G. Ether Days Stored in 5-Gallon Iron Drums 281	 520	 1076	 1370
N-Benzyl-p-aminophenol	16	Nil	Nil	Nil	Nil
Diethylenetriamine	50	Nil	Nil	0.003	0.003
Triethylenetetramine	50	Nil	Nil	0.003	0.003
Tetraethylenepentamine	50	Nil	Nil	0.003	0.003
Morpholine	300	0.007	0.014	0.017	0.013
Ethylenediamine	50	0.006	0.006	0.010	0.069
		Days Stored in 1-Gallon Clear Glass Jugs			
		60	165	281	520
N-Benzyl-p-aminophenol	16	Nil	Nil	Nil	0.001
Diethylenetriamine	50	Nil	Nil	Nil	Nil
Triethylenetetramine	50	Nil	Nil	Nil	Nil[a]
Tetraethylenepentamine	50	Nil	Nil	Nil	Nil[a]
Morpholine	300	Nil	0.012	0.017	0.020
Ethylenediamine	50	0.009	0.020	0.016	0.034

[a] Several small brown tar spots on bottom of glass container.

The rate of peroxidation of the control samples in which the ether was stored in 5-gallon plain iron and coated iron cans, and in 1-gallon glass bottles, is shown by the curves in Figure 1.

Oxygen availability is, of course, one of the controlling factors in the rate of peroxidation of the uninhibited isopropyl ether samples shown in these curves. Accurate quantitative evaluation of this factor would be difficult and no attempt was made to do so. While all of the containers were fitted with screw-cap closures and efforts

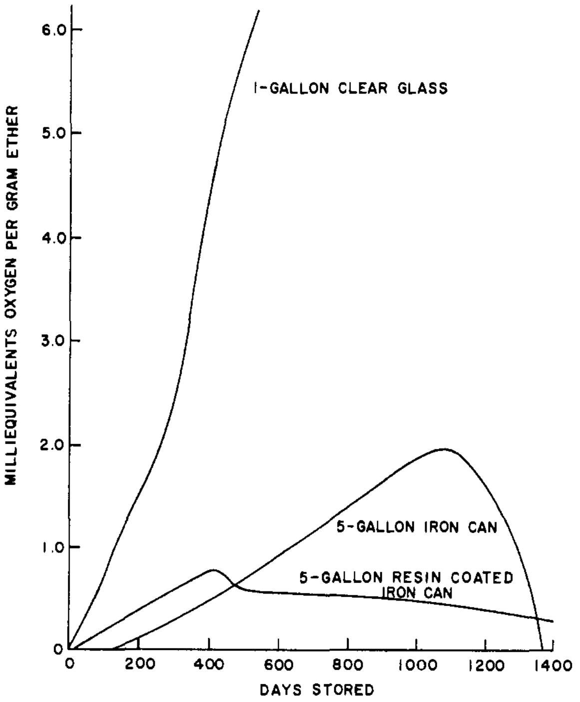


Figure 1. Autoxidation of uninhibited isopropyl ether

were made to close the caps before and between periods of sampling just as they would be in the case of sampling during periods of normal storage, one cannot be sure that some of the containers did not breathe more freely than others, or that more air was not admitted to one container than another during sampling. Because of these possible deviations in available oxygen, the curves in Figure 1 may not be completely interrelated; however, their relationship is such to warrant their use as a reasonable indication of the amount of peroxidation that may be expected in uninhibited ether when it is stored and handled in a normal fashion over prolonged periods of time. The accelerated rate of peroxidation observed for the ether stored in the clear glass container was probably influenced more by the presence of light than by possible differences in the rate of diffusion of air into the container.

Coated containers are now widely used in the chemical industry to protect the purity of refined products in storage, and it was of interest to compare the relative rate of peroxidation of the ether in coated and uncoated iron containers. Again, one cannot be certain that oxygen availability at all times during storage and sampling was the same for these two types of containers. However, for all practical purposes the conditions of storage were the same. Over the prolonged storage period notable differences were observed in the rate of peroxidation of the uninhibited ether stored in these containers. Peroxidation in the plain iron can did not occur until after an appreciable lapse of time (approximately 100 days), while in the coated container there was a steady increase in peroxide content with time from the start of the test. After 400 days of storage there was a steady decline in the peroxide content of the ether stored in the coated container, while the peroxide content of the ether in the plain iron container increased steadily at a fairly rapid rate. The reasons for the particular shape of these curves and the rapid decomposition of peroxide in the plain iron container toward the end of the storage period are not definitely known, but are probably associated with an increase in other impurities in the ether and in the onset of corrosion on the containers. More tests would, of course, have to be conducted to establish reliable trends in the relative rates of peroxidation of the ether in these containers under normal storage conditions.

One of the most interesting phases of the prolonged storage tests in iron containers was the effect of the amines as corrosion inhibitors. At the end of the test the iron can containing ether to which no antioxidant was added was severely corroded and contained a large volume of rust. The coating in the resin-lined can was blistered and spalled under vapor exposure. There was no evidence of corrosion on the cans containing the ether to which triethylenetetramine and *N*-benzyl-*p*-aminophenol were added and only a very slight amount of rust in the liquid exposure of the can containing morpholine. A relatively small amount of rust formed in the vapor space of the can containing ether to which the other amines had been added. The appearance of three of the cans at the conclusion of the tests is shown in Figure 2.

The specification analyses were determined on the ether solutions stored in the iron drums at the end of 520-, 1076-, and 1370-day storage intervals, and at the termination of the storage test in the 1-gallon glass bottles (520 days).

The ether solutions to which the amines were added passed all requirements for refined grade material after 520 days of storage in the iron cans; some failed to pass the requirement on suspended matter only at the end of the 1076-day storage interval, and a few failed to pass the requirement with respect to water content and initial boiling point at the end of the 1370-day storage period. Only one, the ether to which ethylenediamine was added, failed to pass the requirement for maximum peroxide content at the end of this time. Two of the ether solutions, those containing morpholine and ethylenediamine, failed to pass this requirement at the end of the 520 days of storage in glass.

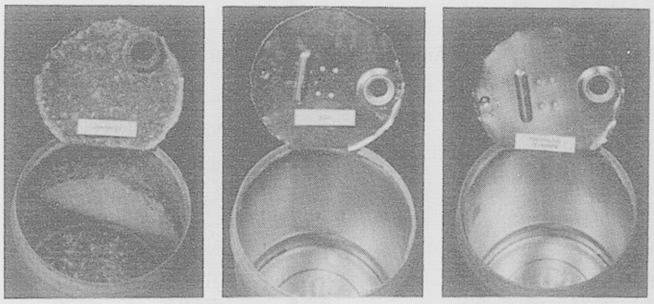


Figure 2. Appearance of 5-gallon iron cans after storage of isopropyl ether for 1370 days

Left. No antioxidant added to ether
Center. Ether contained 16 p.p.m. of *N*-benzyl-*p*-aminophenol
Right. Ether contained 50 p.p.m. of triethylenetetramine

CONCLUSIONS

N-Benzyl-*p*-aminophenol is an excellent preservative of the ether. Several less costly and readily available aliphatic amines, such as diethylenetriamine, triethylenetetramine, and tetraethylenepentamine, may be used with equally good results in preserving this ether in storage. Morpholine and ethylenediamine are effective antioxidants, but do not appear capable of preserving the ether free from peroxides for as long as the higher molecular weight amines.

The results of storage tests on isopropyl ether have suggested the use of these amines as antioxidants and stabilizers for other readily oxidizable organic compounds. The use of very small amounts of these materials as corrosion inhibitors during shipment and prolonged storage of refined chemicals is also indicated by the tests.

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