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STABILIZATION OF ORGANIC PEROXIDES

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This invention relates to a method of stabilizing organic compounds which contain peroxy oxygen. Liquid organic peroxy compounds are often unstable and will decompose upon standing at room temperatures. Some of these compounds will decompose with explosive violence at temperatures slightly in excess of room temperatures. If the compounds are confined in the usual vessels provided for storage or shipment, the heat generated by normal decomposition may cause an elevation in temperature sufficient to cause an explosion. Such dangers have greatly limited the utility of the liquid organic peroxy compounds. Accordingly, one of the purposes of this invention is to provide a method of preventing the spontaneous decomposition of liquid organic peroxy compounds and thereby permit storage for long periods of time without the danger of loss. A further purpose of this invention is to eliminate the danger of explosions and fires in the use, storage, and shipment of liquid organic peroxy compounds.

I have invented a method of stabilizing liquid peroxy compounds which otherwise would decompose spontaneously within a very few minutes under ordinary conditions. By my method it is possible to completely avoid all danger of rapid decomposition or explosion over long periods of time. Many of the peroxy compounds, particularly the low molecular weight percarbonates, are very explosive and must be prepared at very low temperatures to prevent immediate decomposition. In such cases, the use of my invention is particularly advantageous. Many liquid peroxy compounds decompose more slowly and do not present a serious explosion problem. Such compounds decompose at an appreciable rate, however, and this invention has substantial utility in preventing such loss, thereby greatly lengthening the active life of the compounds.

I have found that by adding a small proportion of iodine to a liquid peroxy compound the normal rate of decomposition thereof is greatly retarded and explosion dangers eliminated. The iodine is preferably added in amounts up to 1 percent. Higher proportions of iodine will cause a further improvement in stability. Thus concentrations up to 5 percent may be used. The iodine should ultimately be in solution. It is usually added

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in solid form and dissolved by stirring or agitating the liquid. Normally, colorless liquid peroxy compounds will be colored yellow, orange, or deep red by the dissolved iodine, the coloring depending upon the solubility of iodine in the particular peroxy compound.

The iodine stabilization treatment of the invention is particularly advantageous in that it does not impair the utility of the peroxy compound. Although the presence of iodine may temporarily affect the color of the preparation, it is removed before use, thereby regenerating the pure colorless liquid peroxide compound.

My invention is useful in inhibiting the decomposition of any liquid compound containing peroxy oxygen, for example:

Peroxides	$R-O-O-R$	(A)
Acylperoxides	$R-C(=O)-O-O-C(=O)-R$	(B)
Peroxy dicarbonates	$R-O-C(=O)-O-O-C(=O)-O-R$	(C)
Monoperoxy carbonates	$R-O-O-C(=O)-O-R$	(D)
Diperoxy carbonates	$R-O-O-C(=O)-O-O-R$	(E)

Many peroxy compounds are solids not subject to spontaneous decomposition. Hence, the invention is particularly adapted to treatment of liquid peroxy compounds and especially those in the above classes.

The new stabilization method may be practiced by adding solid iodine to a freshly prepared and purified liquid peroxy compound or the same peroxy compound may be prepared in the presence of iodine. The stabilization method although greatly inhibiting the decomposition frequently does not entirely prevent it. Decomposition proceeds at a very slow rate becoming almost imperceptible at low temperatures. Accordingly, it is desirable to store the stabilized solutions in a refrigerator. This is especially advantageous if the solution is stored in a closed container. Such containers should be vented to the atmosphere to prevent increased pressures within, due to the slow decomposition.

Frequently, the iodine may be only slightly soluble in peroxy compounds or is but slowly dis-

solved therein. Larger quantities of iodine may be incorporated if a water-soluble solvent such as ethyl alcohol is present. This modification of the invention may be practiced by preparing concentrated solutions of iodine in the solvent and adding such solutions to the peroxy compound.

Before use of the stabilized peroxy compounds for most purposes it is necessary to remove the iodine. The stabilized solution is first filtered to remove all traces of solid iodine. The filtered solution is then washed with a dilute water solution of a strong oxidizing agent such as hypochlorous acid and subsequently with water. Frequently it is desirable to follow the hypochlorous acid with a very dilute caustic soda washing which may in turn be followed by a wash of dilute acetic acid. In all instances, the peroxy compounds are ultimately washed with water until neutral to litmus. All washing should be performed with the wash solutions at approximately 0° C. The washed peroxy compounds again become very unstable and should be stored at temperatures of 0° C. or lower. The use of solid carbon dioxide, as a cooling medium, is preferred.

Other methods of removing the iodine will be apparent to the skilled chemist. For example, a very effective removal can be obtained by blowing the filtered stabilized solution with a jet of air for a period of several hours. This will cause vaporization of the dissolved iodine and complete removal thereof. This method of removing iodine should be used at temperatures as low as practicable to avoid excessive vaporization of the peroxy compound. This method is advantageous since the contact of air has an independent stabilizing effect on the percarbonate. Accordingly, as the iodine is removed the danger of spontaneous decomposition and explosion will not return until the air circulation is interrupted. Accordingly, the same equipment used to remove iodine may be used as a temporary storage vessel for the purified peroxy compound prior to use.

Further details of the practice of the invention are set forth in detail in the following examples:

Example I

Approximately one pound of colorless isopropyl percarbonate analyzing 99.4 percent pure was stabilized by adding 4 g. of iodine and shaking until most of the iodine was dissolved. After storage for ten days the stabilized solution was filtered and cooled to approximately 0° C. It was washed with two volumes of water to which was added about 0.1 percent of sodium sulfate for the purpose of facilitating the separation into two liquid phases. The solution was then washed with 1 percent hypochlorous acid which removed practically all of the iodine and left the solution with a faint yellow color which was subsequently removed by washing with water. The colorless solution was then washed successively with 1 percent sodium hydroxide, 1 percent acetic acid, and ultimately with water until neutral to litmus. The colorless isopropyl percarbonate thus produced assayed at 99.6 percent.

A 10 g. sample of the original unstabilized isopropyl percarbonate was permitted to stand at room temperature. In 12 minutes it decomposed with a rapid evolution of gas.

Example II

A sample of ethyl percarbonate containing 1 percent of iodine was stored at room temperature (25 to 30° C.) and analyzed periodically for two weeks. The following results were obtained:

Time, hours	Assay, per cent
0	98.4
72	89.7
114	82.2
209	74.5
258	67.4
330	62.8

A sample of the identical compound except without iodine decomposed violently in less than nine minutes.

Although the invention has been described with respect to certain specific examples it is not intended that the details thereof shall be regarded as limitations upon the scope of the invention except to the extent incorporated in the following claims.

I claim:

1. A method of preventing the decomposition of liquid organic compounds containing peroxy oxygen which comprises adding a small proportion of iodine to the organic peroxy compound.

2. A method of preventing the decomposition of liquid organic compounds containing peroxy oxygen which comprises adding up to 1 percent of iodine to the organic peroxy compound.

3. A method of preventing the decomposition of liquid organic compounds containing peroxy oxygen which comprises dissolving iodine in the peroxy compound.

4. A method of preventing the decomposition of liquid organic compounds containing peroxy oxygen which comprises dissolving up to 1% of iodine in the peroxy compound.

5. A stabilized liquid organic compound containing peroxy oxygen which comprises a liquid organic peroxy compound and iodine.

6. A stabilized liquid organic compound containing peroxy oxygen which comprises a liquid organic peroxy compound and up to 1 percent of iodine.

7. A method of preventing the decomposition of liquid percarbonates which comprises dissolving iodine in said percarbonates.

8. A method of preventing the decomposition of isopropyl percarbonate which comprises dissolving iodine in the isopropyl percarbonate.

9. A stable liquid percarbonate comprising a liquid percarbonate and iodine.

10. A stable isopropyl percarbonate comprising isopropyl percarbonate and iodine.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,335,856	Hooft	Dec. 7, 1943
2,319,576	Agens	May 18, 1943

OTHER REFERENCES

Welland "Annalen der Chamie, Liebigs," vol. 446, pgs. 46, 47 (copy in Patent Office Library, 260–610).