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Reprocessing stored ether to very low

peroxide levels can be accomplished by treating it

with amines or with a variety of inorganic reagents

DESTROYING PEROXIDES OF

ISOPROPYL ETHER

The explosive nature of peroxides of isopropyl ether and the risk of fatal accidents have led to a consumer demand for a product with more stringent peroxide limitations. Some customers now specify a peroxide-free ether, or an isopropyl ether with a peroxide content of no more than a few parts per million. Because of the extreme susceptibility of isopropyl ether to oxidation, it is often difficult for the producer to meet these new requirements. The producer may find it necessary to reprocess stored ether which has acquired some peroxides in order to meet this more exacting grade.

Peroxides of isopropyl ether have a higher boiling point than the ether itself, and the ether therefore cannot be safely dry-distilled unless peroxides are known to be absent. The temperature and concentration at which explosion becomes probable have never been authoritatively stated. Even a very small amount of peroxide may be dangerous, since it is concentrated in the still system.

The need for reprocessing a large volume of isopropyl ether stored at one of our plants led to a laboratory study to find effective and economic means of destroying peroxides. Peroxide content of the stored ether was well below the customary maximum limit, but did not meet the new requirements. It was hoped that peroxides could be converted to harmless substances while using an amount of reagent small enough to have no deleterious effect on ether quality. This goal was not attained—any material which completely destroyed peroxides also appreciably degraded the ether. Subsequent redistillation or dehydration is required to restore the ether to the specifications of a refined product.

Materials tested for their effect on peroxides of isopropyl ether included several amines, used both in undiluted form and as aqueous solutions. Inorganic reagents previously recommended in the literature were also tested. These included solutions of sodium hydroxide, sodium metabisulfite, ferrous sulfate, and stannous chloride. In addition, solid stannous chloride, ferrous sulfate, and sodium metabisulfite were tested.

Results of these tests showed that:

—In a cold washing operation, high concentrations of peroxides were completely removed by treatment with 25% by weight of undiluted triethylenetetramine, and reduced to very low concentrations by treatment with this amount of undiluted diethylenetriamine and propylenediamine.

—When ether which contained peroxides was refluxed in the presence of 25% by weight of undiluted triethylenetetramine and

diethylenetriamine complete removal of the peroxides occurred within one hour.

—Aqueous 20% solutions of hydroxylamine hydrochloride destroyed peroxides when used in cold washing treatments.

—Sodium metabisulfite solution was the most effective of the inorganic reagents tried. This reducing reagent was found to react quickly with the peroxides in isopropyl ether in essentially a stoichiometric manner.

—Stannous chloride was the only inorganic reagent which was effective in the solid form.

Because of other variables that would be introduced, it is not possible from the laboratory experience to choose a single "best" reagent, or to give specific instructions for removal of peroxides by the use of the inorganic reducing agents in plant-scale operations. Plant equipment for conducting the treatment would influence the results, and the peroxide content of the two liquid phases during the mixing operation.

For our purposes, the best system was chosen as cold-washing with sodium metabisulfite solutions. While details of the operations were not given, it was recently reported by the Production Department of the Chemicals Division that isopropyl ether having 0.017 meq. O_2 per gram of ether was successfully treated with 3.0% sodium metabisulfite solution. After treatment and subsequent refining, the peroxide content of the ether was a maximum of 0.0007 meq. O_2 per gram of ether. Stainless steel equipment is preferred for this process.

Effect of Amines on Decomposition of Peroxides

Amines and amine-like compounds are known to be effective antioxidants. One of these chemicals, morpholine, has been successfully used by the Chemicals Division of Union Carbide Corp. to prevent peroxidation of freshly distilled isopropyl ether. Other amines, for example, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine appear to be equally effective as peroxide inhibitors for this ether (6).

The decomposition of peroxides by amines has been reported by a number of investigators. Capp and Hawkins (2) studied the reaction of organic amines with alkaryl hydroperoxides and stated that these peroxides could be converted smoothly into the corresponding alcohol with loss of one atom of oxygen by treatment with many amines. Others (7, 10) have reported on the decomposition of peroxides by amines and have

proposed partial and tentative mechanisms for the reaction. The use of polyalkylene polyamines as activators for peroxide-catalyzed polymerization by decomposition of the peroxide catalyst has been described. Many amines were effective in bringing about rapid polymerization at low temperature (11).

Addition of Undiluted Amines

The effect of undiluted amines on decomposition of the peroxides was first investigated. None of the amines tried in the undiluted state effectively decomposed the peroxides unless added to the ether in relatively large amounts. Typical data obtained for a cold washing process are given in Table I. Triethylenetetramine was the most effective of the many tried (Trial 17, Table I). The peroxides were also removed by refluxing the ether a short period of time with 25% by weight of either diethylenetriamine or triethylenetetramine (Trials 6 and 18, Table I). Ethylenediamine and propylenediamine were less effective peroxide decomposition agents than the amines mentioned above, but results of the studies indicate that these amines also may possibly be used in the undiluted state to remove dangerous amounts of peroxides from isopropyl ether.

The amines, and in particular propylenediamine, appear to be soluble in isopropyl ether to an appreciable extent, so that it would be necessary to separate the amine from the isopropyl ether by distillation after treatment. When the amines are first added to the isopropyl ether, a cloudiness appears in the ether phase and remains for an hour or two after which it disappears. When heated, the ether phase clarifies immediately but becomes cloudy again when the solution is cooled.

This phenomenon is presumably related to the solubility of amine in the ether and the effect of temperature on the solubility.

Effect of Aqueous Amine Solutions

Since a large excess of the pure amines was required for satisfactory destruction of the peroxides, the effect of aqueous solutions was of interest. The results of a cold washing process using aqueous solutions of the amines are shown in Table II. The effect of temperature on decomposition of the peroxides in contact with solutions of a variety of amines is summarized in Table III. The data given in these tables are typical data taken from a large number of experiments that were conducted in an effort to determine the most suitable amine for the purpose. The amount of reagent required to decompose the peroxides can be estimated from the quantities shown.

While the peroxide content of the isopropyl ether was appreciably reduced by cold washing for short periods of time with many of the aqueous amine solutions, only one completely destroyed the peroxides—hydroxylamine hydrochloride. Sufficent data were obtained to indicate that solutions of this amine are effective over a wide range of peroxide concentration. In addition to the data given in Table II, it will be observed from further data shown in Table V that complete decomposition of peroxides in isopropyl ether containing more than 1000 p.p.m. was accomplished by cold washing 3 volumes of the ether for 2 hours with 1 volume of a 10 per cent solution of hydroxylamine hydrochloride.

Hydrazine, like hydroxylamine hydrochloride, is a strong reducing agent. The reaction of this chemical with hydrogen peroxide has been described (7), and it

TABLE I. EFFECT OF UNDILUTED AMINES

| Trial | Amine | | Treatment | Peroxides, Meq. O₂/G. Ether | |
	Name	% Added[a]		Start	End
1	Butylamine	1	Shaken 15 min.; heated 2 hr., 55° C.	0.012	0.012
2		5	Shaken 15 min.	0.036	0.033
3	Diethylenetramine	1	Shaken 15 min.; heated 2 hr., 55° C.	0.012	0.006
4		10	Shaken intermittently, 1 hr.	0.200	0.015
5		25	Shaken intermittently, 1 hr.	0.200	0.003
6		25	Refluxed 1 hr.	0.200	nil
7	Ethylenediamine	3	Shaken 15 min.; quiescent 17 hr.	0.021	0.010
8		10	Shaken intermittently 1 hr.	0.200	0.021
9		25	Shaken intermittently 1 hr.	0.200	0.010
10	Morpholine	5	Refluxed 2 hr.	0.058	0.048
11	Propylenediamine	3	Shaken 15 min.; heated 2 hr., 55° C.	0.012	0.001
12		10	Shaken intermittently, 1 hr.	0.200	0.021
13		25	Shaken intermittently, 1 hr.	0.200	0.001
14	Triethylenetetramine	1	Shaken 15 min.; heated 2 hr., 55° C.	0.012	0.005
15		5	Refluxed, 2 hr.	0.058	0.004
16		10	Shaken intermittently, 1 hr.	0.200	0.018
17		25	Shaken intermittently 1 hr.; quiescent 17 hr.	0.200	nil
18		25	Refluxed, 1 hr.	0.200	nil

[a] Per cent by weight of pure amine added to the isopropyl ether.

was anticipated that the peroxides of isopropyl ether would respond to the action of this reducing agent in a manner analogous to its reaction with hydrogen peroxide.

In attempts to decompose the peroxides in a low-peroxide ether, dilute aqueous solutions of hydrazine had no effect. In fact, in some tests, the peroxides increased during treatment. However, tests using a high-peroxide ether showed that very strong solutions of this reagent appreciably reduced the peroxides. Hydrazine hydrate, a commercial preparation of 85% aqueous hydrazine, when used in excess of the amount of peroxides present, destroyed all but a very small amount of the peroxides. Violent effervescence and evolution of gas occurred, owing to decomposition of both the peroxides and hydrazine. Hydrazine is a very reactive chemical and the hazards of handling this reagent make it a very unlikely candidate for decomposition of peroxides in ethers.

Under conditions in which the peroxidic ether was refluxed in the presence of aqueous 20% amine solutions, the peroxides were completely destroyed when hydroxylamine hydrochloride and triethylenetetramine were used and reduced to low concentrations using diethylenetriamine, diethylaminopropylamine, ethylenediamine, morpholine, propylenediamine, triethanolamine, and tetraethylenepentamine (Table III).

From the laboratory studies it appears that reaction of the amines with the peroxides of isopropyl ether varies with the particular amine used for the purpose, the concentration, and the temperature. The reader who has a special interest in this aspect will find much information on the chemistry involved from the detailed and extensive studies of Hawkins (7) and Tobolsky (10).

Peroxides of variable compositions form in isopropyl ether. Some of the peroxides are more easily decomposed than others. Some, the cyclic peroxides of diacetone and triacetone, which are stated to form in isopropyl ether (9), are claimed to be more dangerously explosive than others. For this reason, continued study may be needed to determine whether certain of the amines will be effective deperoxidation agents under all circumstances.

Experience has been that peroxides often form in isopropyl ether in the latter stages of the refining operation. Peroxidation is a "chain reaction" and proceeds at a rapid pace. Such being the case, the addition of an amine in the ether refining process just prior to the final operation may well retard or prevent autoxidation for appreciable lengths of time. Unpublished laboratory data by the author have clearly indicated the benefits of this procedure on subsequent stability of the isopropyl ether.

Effect of Inorganic Reagents

Because ether peroxides are very unstable and are both oxidizable and reducible, many inorganic reagents have been suggested for purification of ethers. Fisher and Baxter (4) studied the effect on decomposition of peroxides in ethers and dioxane by sodium hydroxide and reducing agents such as metal oxides, powdered zinc, sodium bisulfite, stannous chloride, and ferrous sulfate. Hunter and Downing (8), and Williams (12), in reviewing suggested methods for purification of peroxidic ethers to render them free from explosive hazard. They mention the use of such compounds as powdered iron, mercury, potassium permanganate, aqueous sodium carbonate, ferrous sulfate, sodium metabisulfite and

TABLE II. EFFECT OF COLD WASHING WITH AMINE SOLUTIONS

Trial	Amine Solution	Volume, Ml. Amine, 20% aqueous soln.	Ether	Peroxides, Meq. O₂/G. Ether Start	End Ether	End Amine
1	Butylamine	25	25	0.024	0.009	0.001
2	Diethylenetriamine	25	25	0.024	0.008	Nil
3	Diethylenetriamine[a]	10	25	0.101	0.029	. . .
4	Dipropylenetriamine	25	25	0.024	0.008	Nil
5	Diethylaminopropylamine	30	75	0.004	0.002	0.003
6	Ethylenediamine	25	25	0.024	0.005	0.001
7	Hydrazine	20	60	0.200	0.014	0.004
8	Hydrazine hydrate[a,c]	3	60	0.200	0.001	[b]
9	Hydroxylamine hydrochloride[a]	25	50	0.017	nil	Nil
10	Hydroxylamine hydrochloride	30	75	0.004	nil	Nil
11	Hydroxylamine hydrochloride[a]	20	150	0.097	0.002	Trace
	Hydroxyethylpiperazine[a]	20	50	0.028	0.011	Trace
12	Monoethanolamine	25	25	0.024	0.009	0.001
13	Morpholine[a]	25	50	0.037	0.015	0.006
14	N-Methylmorpholine[a]	20	50	0.035	0.013	. . .
15	Propylenediamine	20	25	0.024	0.009	0.001
16	Triethylenetetramine[a]	25	50	0.037	0.013	Nil
17	Triethylenetetramine	25	25	0.024	0.010	Nil
18	Tetraethylene pentamine[a]	25	50	0.028	0.009	Nil
19	Triethanolamine	25	50	0.036	0.014	0.001

[a] After shaking together with the isopropyl ether these amine solutions remained in contact with the ether overnight (about 17 hours) before analysis for peroxide content. [b] A heavy white precipitate of hydrazine sulfate formed in the sulfuric acid solution used in the peroxide analysis. [c] Eighty-five per cent hydrazine in water. Strong evolution of gas when shaken with the ether.

stannous chloride, and recommend steam distillation of ether over dilute sodium hydroxide solutions as a safe procedure for purification. The United Kingdom Atomic Energy Authority recently investigated the known methods for treating ethyl ether containing high concentrations of peroxides after use in purification of ore solutions, and reported that the best method was to wash the ether with an acid solution of ferrous sulfate (3).

Although sodium hydroxide and sodium carbonate solutions have been suggested as ether peroxide decomposition agents, they were not very effective in removal of the peroxides developed in isopropyl ether under the test conditions employed (Trials 1, 2, 3, and 4, Table IV).

Among the most effective inorganic reagents tried for removal of the peroxides in isopropyl ether were sodium metabisulfite, ferrous sulfate, and stannous chloride. A comparison of the effect of these three reducing agents may be observed from the data of Table IV.

The peroxides of isopropyl ether at either low or high concentrations were quickly and completely removed by washing the ether with cold, very dilute aqueous solutions of sodium metabisulfite. The amount of bisulfite present in the wash water, it was determined, need only be equivalent in amount or slightly in excess of the amount of peroxides calculated to be present in the ether that is being washed (compare amounts of sodium bisulfite and peroxide in Trials 8 and 10, Table IV).

The ease and rapidity by which peroxides were decomposed in isopropyl ether by use of sodium metabisulfite solution are illustrated in the data obtained in the corrosion tests of Table V, where the peroxides in a high-peroxide ether were completely destroyed by stirring 10 volumes of the ether with 1 volume of the aqueous 5% solution for 15 minutes. Some later experiments were conducted to determine the actual time required for decomposition of the peroxides to take place by reaction with dilute sodium metabisulfite solution. In these experiments [data not included in the tables] 200 ml. of a 5% solution of sodium metabisulfite was added to 800 ml. of isopropyl ether containing 0.575 meq. O_2 per gram of ether in a 2-liter Pyrex reaction vessel equipped with an electric stirrer and provided with an access for sampling the ether and water phases. In this case, the amount of bisulfite was only in slight excess of the amount of ether peroxide present. Results of these tests showed that decomposition of the peroxides was very rapid. An appreciable rise in temperature occurred upon addition of the bisulfite solution to the ether (about 10° F.). No peroxides were found in samples of the ether or water phase withdrawn at any of the test intervals down to as low a time interval as 30 seconds. When the peroxide content is high, considerable heat is evolved in the treatment with sodium metabisulfite and the reagent should be added slowly and with cooling.

Larger quantities of ferrous sulfate and stannous chloride in the form of their aqueous solutions are re-

TABLE III. EFFECT OF REFLUXING WITH AMINE SOLUTIONS

Trial	Amine Solution	Peroxides, Meq.O_2/G. Ether		
			After Reflux[a]	
		Start	Ether	Water
1	Butylamine	0.036	0.009	0.001
2	Diethylenetriamine	0.036	0.003	Nil
3	Dipropylenetriamine	0.058	0.004	Nil
4	Diethylaminopropylamine	0.004	0.001	Nil
5	Ethylenediamine	0.036	0.003	Nil
	Hydroxylamine hydrochloride	0.210	0.010	Nil
6	Hydroxylamine hydrochloride	0.004	Nil	Nil
7	Hydroxyethyl piperazine	0.035	0.004	Trace
8	Morpholine	0.024	0.003	0.001
9	N-Methylmorpholine	0.058	0.008	0.004
10	N-Aminopropylmorpholine	0.058	0.005	Nil
11	N-Aminoethylpiperazine	0.058	0.007	Nil
12	Propylenediamine	0.034	0.001	0.001
13	Triethanolamine	0.052	0.002	0.001
14	Tetraethylenepentamine	0.035	0.003	Nil
15	Triethylenetetramine	0.036	0.002	Nil
16	Triethylenetetramine	0.101	Nil	Nil
17	Triethylenetetramine	0.210	Nil	Nil

[a] One volume of 20% aqueous amine solution was refluxed for two hours with two and one-half volumes of peroxidic isopropyl ether.

quired to remove a given amount of peroxides in isopropyl ether than are required to destroy the peroxides using aqueous sodium metabisulfite. Estimates made from data given in Table IV indicate that these reagents must be used in excess of about five times the amount of peroxides present.

It will be observed that the peroxides of isopropyl ether were destroyed by shaking the ether with stannous chloride in solid form. Sodium metabisulfite and ferrous sulfate did not decompose peroxides when used in the solid state.

The mechanism by which the peroxides are removed by treatment with inorganic reducing agents is stated in its simplest form to be that of reaction of the oxygen of the peroxide with the reducing agent, the reagent being simultaneously oxidized (3). When freshly prepared, aqueous ferrous sulfate solution is a pale green color. After shaking with the peroxidized ether, oxidation of the ferrous ion soon occurred as indicated by a brown coloration of the solution and precipitation of finely divided red ferric hydroxide on the sides of the reaction flask. A very fine white precipitate of tin oxide (SnO_2) or stannic hydroxide formed when the stannous chloride was first added to the ether. This precipitate coagulates to some extent with continued shaking but is difficult to remove by filtration.

For removal of peroxides, one should consider both the concentration of the reducing solution, and the ratio of volume used to that of the ether that is being

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purified. In some cases it may be advantageous to use a weak solution and a large volume to provide better contact. In other instances, more concentrated solutions of the reducing agent may be required to provide more reducing activity. It appears that very weak solutions of sodium metabisulfite effectively destroy the peroxides, while stronger solutions of stannous chloride and ferrous sulfate are more effective than weaker solutions.

Results of the comparative data in Tables IV and V strongly indicated that the bisulfite would be most effective and economical for the purpose. Sodium metabisulfite is more costly than the ferrous sulfate, the cost of this reagent being approximately $14 per 100 pounds as compared with $7.00 per 100 pounds for ferrous sulfate, but it is indicated that only about $1/5$ as much bisulfite as ferrous sulfate and stannous chloride would be needed for treatment of peroxidic isopropyl ether. Stannous chloride is quite costly in comparison with the other two reducing agents, its cost being about $127 per 100 pounds.

Results of the experiments conducted in the laboratory provide a reasonable basis for plant-scale operations. As indicated in the data of Table V, where a large volume of isopropyl ether was treated in corrosion tests, good success should be obtained by cold washing the ether in a mixing tank with 3 to 5% aqueous sodium metabisulfite solution using 1 volume of the bisulfite solution in 10 volumes of ether. The amount of sodium metabisulfite present in the wash water should be equivalent to or slightly in excess of the ether-peroxide present. Intimate mixing of the ether and bisulfite-water phase need not be continued more than a few minutes.

It should be mentioned that sulfur dioxide, a decomposition product of sodium metabisulfite, is slightly soluble in isopropyl ether. In the iodometric method of analysis used for determining the peroxide content of the isopropyl ether this compound will reduce iodine that is released from the potassium iodide reagent by the peroxides causing low results. In order to be certain, therefore, that all of the peroxides have been removed by treatment with the bisulfite solution, the ether should be washed with dilute sodium hydroxide solution or with water alone to remove this impurity before being analyzed for peroxides.

If other reducing reagents, ferrous sulfate or stannous chloride, are preferred for some reason, it is indicated that reprocessing of the ether could be conducted on a plant scale as indicated above for the bisulfite treatment with the modification that the amount of reducing agent in the wash solution should be 5 to 10 times that of the calculated amount of peroxides present in the ether that is being purified. Intimate mixing of the aqueous phase and ether phase should be continued in this case for at least 15 minutes, as far as is known.

As in the case of the treatments using amines, the purity of refined isopropyl ether is appreciably degraded by treatment with the inorganic reagents. The limits of specific gravity, distillation range, water content, and acidity, in some instances, were affected most by the treatments, and subsequent redistillation or dehydration is required to restore the ether to the specifications of a refined product.

TABLE IV. EFFECT OF AQUEOUS SOLUTIONS OF INORGANIC REAGENTS

| | | Volume, Ml. | | Peroxides, Meq. O_2/G. Ether | | |
| | Reagent Name | | | | After Treatment[a] | |
Trial		Reagent	Ether	Start	Ether	Water
1	10% Sodium hydroxide	10	50	0.023	0.006	...
2	20% Sodium hydroxide	25	50	0.028	0.012	0.007
3	20% Sodium hydroxide[b]	20	50	0.101	0.017	0.002
4	20% Sodium carbonate[b]	30	60	0.200	0.037	0.013
5	1% Sodium metabisulfite	10	80	0.011	Nil	Nil
6	3% Sodium metabisulfite	15	75	0.220	Nil	Nil
7	5% Sodium metabisulfite	2	50	0.081	Nil	...
8	5% Sodium metabisulfite	3.3	50	0.152	Nil	...
9	5% Sodium metabisulfite	5	50	0.318	0.017	0.005
10	5% Sodium metabisulfite	7	50	0.318	Nil	Nil
11	5% Ferrous sulfate	15	50	0.318	0.017	c
12	5% Ferrous sulfate	20	50	0.314	0.007	c
13	5% Ferrous sulfate	16	50	0.152	0.001	c
14	5% Ferrous sulfate	3	50	0.027	Nil	c
15	20% Ferrous sulfate	10	50	0.041	Nil	c
16	5% Stannous chloride	7	50	0.314	0.009	0.138
17	5% Stannous chloride	20	50	0.314	0.001	Nil
18	5% Stannous chloride	35	50	0.314	Nil	Nil
19	20% Stannous chloride	10	50	0.041	Nil	Nil
20	Solid stannous chloride	1.4 g.	40	0.338	0.005	...
21	Solid stannous chloride	2.0 g.	50	0.368	Nil	...

[a] *Treatment consisted of vigorously shaking the ether and reagent together in a small bottle for 15 minutes.* [b] *Refluxed two hours.* [c] *The ferric ion liberates iodine from the potassium iodide reagent, interfering with the analysis for peroxides in the water layer.*

TABLE V. CORROSION OF METALS

Treatment Conditions	Aqueous 5% Sodium Bisulfite				Aqueous 10% Hydroxylamine Hydrochloride	
Vol. reagent, ml.	120		120		250	
Isopropyl ether, vol. ml.	1200		1200		800	
Peroxides start, meq. O_2/g. ether	0.179		0.179		0.037	
Peroxides end, meq. O_2/g. ether	Nil[a]		Nil[a]		Nil[b]	
Time of treatment, hr.	2		66		4	
Corrosion Rate of Metals, Inch/Year	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
Mild steel	0.654[c]	0.283[c]	0.406	0.013	3.850	0.625
Copper	0.026	0.114	0.029	0.054	0.064	0.150
Aluminum 3003	0.035	Nil[d]	0.019	0.011	6.150[e]	Nil
Stainless steel type 304	Nil	Nil	Nil	Nil	Nil	Nil

[a] The peroxide content nil after agitating the solution 15 min. [b] The peroxide content at the end of 1 hr. was 0.001 meq. O_2/g. ether; nil after agitating the solution 2 hr. [c] Black deposit on metal; pitted. [d] Shallow pitting. [e] Deeply etched; heavy corrosion deposit; solution contaminated with metal salts.

Materials of Construction

Corrosion tests were conducted on a few of the common materials of construction using one of the inorganic reagents that would most likely be used for the peroxide destruction, sodium metabisulfite, and one of the amines, hydroxylamine hydrochloride, an effective agent and probably the most corrosive of the amines tried for this purpose.

Results of these tests indicated that for the short intervals of time required for the peroxide conversion using sodium metabisulfite solutions, any of the common materials of construction could be used. For continuous operation in this service or for prolonged periods of time, appreciable damage to mild steel, copper, or aluminum equipment would be expected. Stainless steel type 304 was unattacked during the laboratory test and would be the preferred material of construction for the bisulfite washing operation.

Corrosive attack in treatments using aqueous 10% hydroxylamine hydrochloride solution would be too severe to conduct in mild steel or aluminum equipment. Copper would be suitable for occasional treatments. Stainless steel type 304 was not attacked during an initial 4-hour exposure in the rapidly agitated isopropyl ether-amine hydrochloride solution and would be the preferred material for the deperoxidation treatments using this reagent also. Treatment of the isopropyl ether with any of the other aqueous amine solutions tried could very likely be done satisfactorily in mild steel or copper, but not in aluminum. Aluminum is rapidly corroded during initial exposures in nearly all dilute amine solutions. Data on the corrosion resistance of the metal by the peroxide decomposition reagents are summarized in Table V.

Experimental

Refined isopropyl ether meeting all specification requirements was used to prepare peroxidized ether for the investigation.

Autoxidation of the isopropyl ether did not proceed readily as anticipated by simple aeration. The best method used for this purpose was to repackage the isopropyl ether in variously sized, clear glass, screw-cap bottles. The screw caps were not tightened so as to provide access of air to the ether, and to avoid the possible hazard of explosions arising when the tightened caps were removed from concentration of the peroxides around the closure. The containers were set aside on the laboratory shelf. Peroxides at various levels of concentration developed in the ether depending upon size of the container, position of exposure with respect to light, and time of exposure.

Treatment of the ether with the various peroxide decomposition reagents in cold washing operations usually consisted in shaking a small measured volume of the isopropyl ether of known peroxide content with a known amount of the reagent in small screw-cap bottles, the peroxide content being determined again at the end of the experiment. In some tests larger quantities of isopropyl ether and reagent were agitated rapidly with an electric stirrer in glass containers of suitable size and samples of the ether and water phase withdrawn at various time intervals for peroxide analysis.

The peroxide was determined by addition of potassium iodide reagent to the ether solutions just previously acidified with dilute sulfuric acid solution, and titration of the liberated iodine with $0.1N$ sodium thiosulfate.

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