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Ministry of Supply
DIVISION OF ATOMIC ENERGY (PRODUCTION)

THE REMOVAL OF PEROXIDES FROM ETHER

by

J. A. DUKES

Research and Development Branch, Springfields Works

Date of Manuscript 13 December, 1951

Reprinted by

United Kingdom Atomic Energy Authority, Industrial Group Headquarters
Risley, Warrington, Lancashire

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This note reviews the known methods for treating ethyl ether used at Springfields, for the removal of peroxide compounds which have explosive properties. The best method appears to be to wash the high-peroxide ether with an acid solution of ferrous sulphate.

The review was made in early 1951 because the Development organisation was at that time engaged on tests of new ether purification processes. This development work is suspended but it still occurs that high peroxide concentrations are met with in the full scale Factory process. It is thought that a wider knowledge of the literature may help in avoiding dangerous occurrences.

1. THE FORMATION OF PEROXIDES.

The distillation of ethyl ether, and of many of its homologues, has long been known to concentrate and accelerate the formation of impurities and to give rise to explosion risks. The impurities found in ether under the ordinary conditions of usage are recorded as including acetic acid, formic acid, acetaldehyde, hydrogen peroxide, di-ethyl peroxide (C_2H_5)₂O₂, monoacetaldehyde hydrogen peroxide, di-acetaldehyde hydrogen peroxide, vinyl ethyl ether and vinyl alcohol⁽²⁾. Ethyl nitrate is also said to be formed under the special conditions of distilling ether from concentrated solutions of nitrates⁽³⁾. The chemistry of formation of many of the peroxide compounds is not established but the conditions favouring their formation have been frequently stated. They include atmospheric oxidation, exposure to ultraviolet light, heating and the absence of certain known anti-oxidants.

The anti-oxidants or inhibitors which suppress the formation of ether peroxides comprise, interalia, hydroquinone, diphenylamine, alpha and beta naphthols⁽⁴⁾ (5). None of these compounds are known to be present in the ether used at Springfields nor is it likely that they could be effectively used in the Factory process. Work carried out by the Springfields branch of Chemical Inspectorate in December 1948⁽⁶⁾ has confirmed that an increase in density of nitrate solutions yields a marked increase in the peroxide content of the distillate during ether-stripping, especially when the solution boiling point rises from 44°C to 80-90°C.

These features of the formation of ether peroxides are recognised in the appropriate Operational Memorandum for the Ether Plant and a procedure is laid down for ensuring the minimum risk of peroxide formation. At one stage in the standard procedure for operation of the ether purification process in Building A.17, peroxide tests have to be made at least at 15 minute intervals and the results reported to Plant operators for immediate action with only a few minutes allowed for carrying out the test.

The formation of peroxides can therefore be regarded as an unavoidable feature of the process as at present operated. There is evidence, moreover, that the project for direct ether purification of ore solutions may give peroxides in greater concentrations and with greater frequency still; this feature being one which was being studied in pilot scale experiments.

II. THE HAZARDS OF PEROXIDES.

The risks attached to the handling of ether-peroxides in glass-ware laboratory apparatus have frequently been described⁽⁴⁾ (7) but no record can be found of any authority stating the concentration or the temperature at which explosion becomes probable. Vibration and the presence of oxidisable matter clearly have an effect on the safe limits. Experiments have been carried out, *in vitro*, with concentrations up to 350 p.p.m. at C.I., Springfields⁽⁶⁾ and it is said in a report originating in I.C.I. (3) that peroxide does not lead to special danger (in the large scale preparation of pure U_3O_8) unless it exceeds 1,000 p.p.m. It was, however, recognised to be American practice to hold the peroxide content

below 10 p.p.m. during the other extraction process. This is the level which Springfields regard as the normal maximum for the extraction process.

Peroxide values inevitably rise steeply during the stripping of ether from mother liquors and extractions liquors and an upper limit of 70 p.p.m. is set for recovered ether returned to ether storage. Above 70 p.p.m. peroxides the ether is drained off into Winchesters and discarded. Above 100 p.p.m. the ether-stripping process is stopped and the contents of the still (though they may include some unrecovered ether, with ether peroxide) are discharged for recovery of their uranium value.

It has also been reported that ether peroxides are poisonous, but since their vapour pressure is much lower than that of ether itself the toxic risk is presumably slight except when ether is used for anaesthetic purposes.

III ETHYL NITRITE.

(3) It is known that ethyl nitrite is formed under the same class of conditions as those which give rise to ether peroxides. It is not clear how this ethyl nitrite is formed, since the usual laboratory preparative method is to react concentrated nitric acid with a mixture of alcohol and sulphuric acid and to distil off in the presence of copper. The product is a constituent of "sweet spirit of nitre". Many textbooks on organic chemistry make no reference to the explosive properties of alkyl nitrites and Sudborough's "Fernthsens" for example states (though with some ambiguity) that it is the isomeric nitro-derivatives which "occasionally explode when quickly heated". An excellent Canadian study (14) of the hazards in using diethyl ether, with very extensive references, makes no mention of ethyl nitrite at all although it states that "mixtures of ether, HNO_3 and H_2SO_4 (presumably concentrated) are supposed to be explosive".

The only evidence so far found that ethyl nitrite carries the same explosive risks as peroxides is in an early textbook (8) but the matter does not seem to have received very wide attention. This is perhaps because ether peroxides can be formed under a variety of conditions whereas the presence of nitro-compounds is clearly necessary for the formation of ethyl nitrite.

The standard test-method employed at Springfields Factory does not distinguish between peroxides and nitrite (9). The separate determination of peroxides and nitrite has been studied at A.E.R.E. in connection with Butex (10) and a technique described by Nozaki (11) is said to be applicable to ether.

So long as it is accepted that nitrite is as hazardous as peroxide it is actually an advantage that the standard test-method allows no distinction to be made. The process for the recovery of ether must therefore be judged on its ability to remove both peroxides and nitrite. Even if it could be shown that ethyl nitrite is not in fact dangerous it is unlikely that a sufficiently rapid test-method could be devised for peroxides alone, in the short time allowable for these process-control tests.

IV. REVIEW OF PREVIOUS WORK ON PEROXIDE REMOVAL.

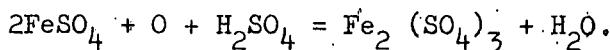
Suggestions were made in October, 1949, by Chemical Inspectorate, Springfields, that peroxides should be removed from ether by treatment with solid sodium hydroxide, at normal temperatures (12). It appears that this lead was not followed up at the time only because of the pressure of other work. Nine different reagents had been tried; FeSO_4 crystals, FeSO_4 with H_2SO_4 , active charcoal, MnO_2 , NaOH , KOH , hydrazine sulphate, Na_2CO_3 and lime, all in the solid state. FeSO_4 would have been quite effective as an aqueous solution but the desire at the time was for a solid reagent. The laboratory-scale experiments of C.I. showed that peroxides could be reduced from 300 p.p.m. to 10 p.p.m. in $2\frac{1}{2}$ hours by stirring cold ether with solid NaOH . It is presumed that a great excess of NaOH was used, but even so the

cost was regarded as being negligible. Therefore only the caustic alkalies appeared worthy of special recommendation at that time.

It was observed that sodium and potassium hydroxides became coated with resinous polymerisation products when they were used for the removal of peroxides. The hazards attached to these unidentified polymers are not known and this factor involves further work before the alkalies can be recommended for large-scale use. It has been reported (14) that peroxides lose their excess oxygen on contact with NaOH, but this is hardly compatible with the formation of resinous polymers.

It has been found by more recent confirmatory tests with 200 gms. of lump caustic soda per 10 litres of ether (13) that it is desirable to wash the ether with water after treatment to extract suspended alkali particles. There is thus no point in working with dry solid reagents for the removal of peroxides and the use of ferrous sulphate solutions, for example, becomes possible.

The reaction of the oxygen of the peroxides with acid ferrous sulphate solution may be written thus :-



The heat of reaction is calculated, for dilute solutions and assuming no heat of decomposition for the peroxides liberating oxygen, as of the order of 35 K cals/gm. formula weight. The effect of this exothermic reaction may be appreciable.

A remarkably successful ad hoc experiment by Production operators showed, in November, 1950, that borehole water was effective in removing the peroxides from ether which had attained the unusually high level of 40 p.p.m. in the extraction plate. Borehole waters are sometimes quite rich in ferrous iron but samples taken in September 1950 show Springfields borehole supplies to be of the order of only 0.5 p.p.m. soluble Fe. Ferrous and ferric iron were not separately determined. It was therefore presumably because of the decomposition by water, rather than by reduction with the ferrous ion, that this recovery of the ether in use at the time was affected.

The most elegant technique for the complete purification of dangerously contaminated ether is undoubtedly that described by Werner (2). It comprises the shaking together of $\frac{1}{2}$ litre of ether with 30 mls. of water containing 4 gms. of dissolved AgNO_3 , then adding 50 mls. of 4% NaOH solution and shaking vigorously for a further 5-6 minutes. Peroxides are destroyed, aldehydes and unsaturated compounds are oxidised to their corresponding acids, and acids are neutralised by the NaOH. It is not necessary to distil the purified ether for a final separation; a simple filtration gives a product with a negative reaction even to Jorissen's test which detects as little as $2\frac{1}{2}$ p.p.m. of peroxides with certainty.

Werner's method is too complicated, and is needlessly expensive in reagents, for large scale operation at Springfields. As alternatives and in addition to the technique tried by C.I. and already referred to above, there remain two which are of passing interest.

One is adsorption in alumina, described by Dasler and Bauer in 1946 (15). This does not seem to be strikingly effective and, in any case, leaves a presumably dangerous concentrate of peroxides in the alumina which may not in practice eliminate all hazards in plant operation. It is believed, however, that the technique has been of value in treating "Butex" where the peroxide does not lead to an explosive hazard.

The other method which is of interest consists of passing the ether over a freshly-prepared zinc-copper couple bed. This is described by

Fierz-David (7) who claimed that it gave an instantaneous reduction of peroxides. It could not be applied to large-scale operation, however, without some prior development work on materials of construction for the plant and on the transfer of undesirable metallic impurities into the ether.

Other investigators have already found that ferrous sulphate solution, with or without the addition of H_2SO_4 , is effective in removing peroxides. E.C.Williams of Shell Development Company published a note "Explosions arising from Ethers" (to which reference has already been made) (4) stating, "Peroxides are destroyed by treatment with ferrous sulphate.....". The context implies the use of $FeSO_4$ solution. Brandt (16) had previously described the use of acidified $FeSO_4$ solution, and similar references are made in the Canadian report on "Hazards in using Diethyl Ether" already referred to (14).

The routine test for determining the concentration of peroxides in ether at Springfields depends upon the oxidation of the ferrous ion. Treatment of ether with a ferrous solution must therefore, under the right conditions, give a zero-test.

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APPENDIX 1.

LITERATURE REFERENCES.

Ref. No.

- (1) Lofthouse and Armstrong; Report No. R/GC/2359 (BR691) and see also "Operational Memorandum No.9; The handling of Ether". dated 11.5.1948.
- (2) Werner; "Analyst"; 58 335(1933)
- (3) Walthen; Report No. R/GC/1047/18 (BR 226)
- (4) Williams; "Chem. and Ind."; 55, 580 (1936)
- (5) Reimers; "Quart. J. Pharm."; 19 172 (1946).
- (6) Analytical Report (C.I., Springfields) H. Mason to Dr. Rogan; 8.12.1948.
- (7) Hans Ed. Fierz-David; "Die Gefahr der Aetherperoxyde", "Chimia"; 1, 247 (1947).
- (8) Richter, "Organic Chemistry" p.144, quoted by Walthen (3).
- (9) SDC 27; Springfields Chemical Development Committee; 20.9.1950.
- (10) Memorandum A.E.R.E. C/M 66.
- (11) Nozaki; "Ind. Eng. Chem."; 18 533 (1946)
- (12) Plant Development (C.I.) Services Report, "The reduction of Ether Peroxide"; H. Mason 14.10.1948.
- (13) Springfields Development, unpublished work; Record Book References D 55 and D 60; December, 1950.
- (14) Wilk; "Hazards in using Diethyl Ether"; Nat. Res. Council Canada Report No. XI-7; 28.2.1947.
- (15) Dasler & Bauer; "Ind. Eng. Chem. (Anal.)"; January 1946.
- (16) Brandt; "Chem. Zeit.>"; 51 981 (1927) quoted by Fierz-David, (7).