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REMOVAL OF ALDEHYDES FROM ETHYLENE OXIDE

David I. Randall, New Vernon, and Eldred Welch, Westfield, N.J., assignors to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware

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3 Claims. (Cl. 260—348)

This application is a continuation of our application Serial No. 74,474, filed on December 8, 1960, now abandoned.

The present invention relates to a new process of removing aldehydes from ethylene oxide.

Ethylene oxide, as produced commercially from the oxidation of ethylene, contains from 500 to 600 p.p.m. of the lower aldehydes such as formaldehyde and acetaldehyde which are commonly referred to and expressed as acetaldehyde. Inasmuch as these aldehydes are undesirable for certain uses of ethylene oxide, it is very important to reduce them to the lowest practical level. This can be accomplished to some extent by rectification.

However, to obtain a low aldehyde content to below about 60 p.p.m., large rectification equipment is needed and as a consequence makes the process very expensive.

It is the particular object of the present invention to provide a new process of removing aldehydes from ethylene oxide.

Other objects and advantages will be more clearly apparent from the following description.

We have found that the aldehyde content, formaldehyde anc acetaldehyde, expressed as acetaldehyde, of commercial grade ethylene oxide, is readily reduced to 10 p.p.m. or less by treatment thereof with an alkali metal borohydride such as the sodium or potassium borohydride. Either the solid, dispersed or dissolved borohydride is satisfgactory in our process. However, from an economical viewpoint, we prefer to employ commercially available solutions such as alkali metal borohydride dissolved in either sodium or potassium hydroxide. The commercially available solution which is particularly adaptable for our process contains 12% of sodium borohydride in a 40% aqueous solution of sodium hydroxide. This solution is much less expensive than the solid material because no isolation of the desired product during manufacture is required. Such a solution when mixed with liquid ethylene oxide reduces the aldehydes to the corresponding alcohols. The more effective and desired procedure of using the alkali metal borohydrides in accordance with our process is either as a dispersion or solution thereof in an inert liquid such as a lower alkyl alcohol, i.e., methanol, ethanol, propanol, butanol and the like or an alkylene glycol such as ethylene glycol, propylene glycol and the like. By this procedure, we found that it is possible to realize almost 100% reduction of the aldehyde content to the corresponding alcohol, i.e., methanol and ethanol.

The method for determining the formaldehyde and acetaldehyde content of commercial ethylene oxide, expressed as acetaldehyde, is the conventional one which consists briefly of adding an excess of a standard sodium bisulfite solution to a water solution of the ethylene oxide. The aldehydes present form the bisulfite addition compound. The amount of unreacted bisulfite is then determined by titrating with a standard iodine solution. Since it is known that aldehydes and sodium bisulfite react in a 1:1 molar ratio, the aldehyde content of the ethylene oxide is easily determined from the amount of bisulfite which reacted. This same analytical procedure is employed for determining the aldehyde content,

expressed as acetaldehyde, of the ethylene oxide following treatment with the alkali metal borohydride.

The manner in which an alkali borohydride reacts with formaldehyde and acetaldehyde is illustrated by the following equation:

$$NaBH_4+4CH_2O+2H_2O\rightarrow 4CH_3OH+NaBO_2$$
$$NaBH_4+4CH_3CHO+2H_2O\rightarrow 4CH_3CH_2OH+NaBO_2$$

Thus, it is evident that the amount of alkali metal borohydride to be employed depends upon the aldehyde content of the ethylene oxide to be treated. During our experimentation with the process of the present invention, we found that between about 50% and 100% of the theoretical quantity of the borohydride charged is used for the reduction of aldehydes to the corresponding alcohols. This means that for each 1000 pounds of ethylene oxide containing 70 p.p.m. aldehyde expressed as acetaldehyde between 0.013 and 0.026 pound of sodium borohydride, either as solid dispersion or solution, are required to reduce the aldehyde content to 10 p.p.m. or less.

In practicing our invention, the chemical grade of ethylene oxide is analyzed for the aldehyde content (formaldehyde and acetaldehyde expressed as acetaldehyde) and then chilled to a temperature of −10 to 10° C. To the liquid ethylene oxide is added, with agitation, the requisite amount of alkali metal borohydride either as the solid, in solution or dispersion, as above noted. Following the addition, the solution is agitated at the low temperature for a period of time ranging from 5 to 60 minutes. Thereafter the liquid is filtered, to remove the alkali metal borate, through a low temperature gravity funnel such as, for example, a conventional funnel the outer surface of which is surrounded by ice or other refrigerating medium such as alcohol or acetone containing solid particles of carbon dioxide. The filtered liquid ethylene oxide is then analyzed for residual aldehyde content.

During the initial treatment of the liquid ethylene oxide with the alkali metal borohydride, the ensuing solution is turbed. This is readily remedied, as noted above, by a simple filtration while employing a cold gravity funnel and ordinary filter paper or cloth, yielding a clear filtrate. When the filtrate is allowed to stand, even at a temperature such as a −10° C., a gelatinous white sediment forms, the amount of which increases with time. This sediment appears to be a polymer formed from the ethylene oxide because of the effect of the caustic present. It is known that caustic catalyzes the polymerization of alkylene oxides to form polyethers. However, to avoid the formation of said sediment, we found that if the treated ethylene oxide, prior to filtration, is neutralized with any conventional inorganic or organic acid and the neutralized liquid filtered, a clear liquid filtrate is obtained which does not form a precipitate on storage. The small amount of the alkali metal salts present in the liquid ethylene oxide, together with the alcohols, is insignificant and will have no effect on the ethylene oxide regardless of the purpose of which it is used. The acid employed for such neutralization is preferably an organic one, such as, for example, formic, acetic, propionic, and the like. In this connection, it is to be noted that the nature or character of the acid is immaterial so long as it is soluble in the treated liquid ethylene oxide, i.e., the reaction mixture.

In the case where it is desirable to produce substantially chemically pure ethylene oxide, the liquid reaction mixture as such prior to filtration, subsequent to filtration and following neutralization and filtration may be subjected to conventional rectification.

The following examples will illustrate the process of removing aldehydes from ethylene oxide.

Example I

To a 500 cc. flask immersed in an ice bath, there were charged 206 grams of ethylene oxide containing 105 p.p.m. of aldehydes expressed as acetaldehyde. The liquid was agitated and from a micropipette was added 0.02 cc. of aqueous sodium borohydride solution of a specific gravity of 1.39 and containing 11.59% of sodium borohydride and 41.75 of caustic soda. The sodium borohydride content of the solution was theoretically equivalent to 72.5 p.p.m. of aldehydes in the ethylene oxide charge. After agitating the liquid mixture at the ice-bath temperature for 40 minutes, the liquid was filtered through an ice cold gravity funnel.

The ethylene oxide analyzed 60 p.p.m. of acetaldehyde which represents 62% of the theoretical amount of the sodium borohydride used. After storage at −10° C. for less than 2 days, a white gelatinous precipitate was formed. The precipitate was removed by cold filtration yielding a clear filtrate.

Example II

The aqueous sodium borohydride solution of Example I was converted into a slurry by diluting 2 grams thereof to 10 cc. with ethanol. To 200 grams of ice cold ethylene oxide containing 130 p.p.m. of aldehydes, expressed as acetaldehydes, was added 0.24 cc. of the slurry. After agitating for 30 minutes at 0–5° C.; there was added 0.030 cc. of glacial acetic acid and agitation continued for 5 minutes. The turbid reaction mixture was filtered. Analysis showed 30 p.p.m. aldehyde. The theoretical amount of sodium borohydride utilized in the conversion of the aldehydes in the corresponding alcohols was 77%. The liquid ethylene oxide was clear with no precipitate after storage for more than a month.

Example III

The procedure of Example II was repeated while employing 200 grams of ethylene oxide containing 70 p.p.m. of aldehydes, expressed as acetaldehyde, 0.28 cc. of the sodium borohydride slurry and 0.034 cc. of glacial acetic acid which was added from a micropipette. The resulting ethylene oxide contained 10 p.p.m. of aldehyde and was clear after a storage period of 16 days at 5° C.

Example IV

The procedure of Example II was repeated, except the agitation time was 60 minutes, while employing 200 grams of ethylene oxide containing 69 p.p.m. aldehyde, expressed as acetaldehyde, 0.11 cc. of the sodium borohydride slurry and .015 cc. acetic acid. The resulting ethylene oxide contained "nil" p.p.m. aldehyde by the standard analysis.

Example V

The procedure of Example II was repeated, except the agitation time was 5 minutes, while employing 200 grams of ethylene oxide containing 69 p.p.m. aldehyde, expressed as acetaldehyde, 0.273 cc. of the sodium borohydride slurry and 0.05 cc. acetic acid. The resulting ethylene oxide contained 2 p.p.m. aldehyde.

Example VI

The procedure of Example II was repeated while employing 200 grams of ethylene oxide containing 47 p.p.m. aldehydes, 0.185 cc. of the sodium borohydride slurry and 0.009 cc. acetic acid. The resulting ethylene oxide contained "nil" p.p.m. aldehydes by the standard analysis.

We claim:

1. The process of removing aldehydes selected from the class consisting of formaldehyde and acetaldehyde from ethylene oxide which consists of treating liquid ethylene oxide at a temperature ranging from −10° to 10° C. with a reducing amount ranging between about 50% and 100% of the amount of an alkali metal borohydride theoretically required to reduce the said aldehydes to the corresponding alcohols for a period of time ranging from 5 to 60 minutes, and thereupon neutralizing the treated liquid ethylene oxide with an organic carboxylic acid of from 1 to 3 carbon atoms and removing the alkali metal salt of said acid and the borate by filtration.

2. The process according to claim 1 wherein the alkali metal borohydride is sodium borohydride.

3. The process according to claim 1 wherein the alkali metal borohydride is potassium borohydride.

References Cited by the Examiner

UNITED STATES PATENTS

2,248,635	7/41	Marple et al.	260—348.6
2,550,847	5/51	Mitchell et al.	260—348
2,697,104	12/54	Lowe et al.	260—348
2,780,643	2/57	Buchner	260—475
2,841,595	7/58	Pezzaglia	260—348.6
2,867,651	1/59	Wise	260—475
3,041,356	6/62	Payne et al.	260—348

FOREIGN PATENTS

827,450	2/60	Great Britain.

OTHER REFERENCES

"Chem. & Eng. News," vol. 37, pp. 49 and 50, April 20, 1959.

WALTER A. MODANCE, *Primary Examiner.*

NICHOLAS S. RIZZO, JOHN D. RANDOLPH,
Examiners.