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Literature Review of Mechanisms of Interaction of
Ethylene Oxide and Organic and Inorganic Materials

by

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ABSTRACT

A search has been conducted of literature published after January 1962 to obtain information on the mechanism of interaction of ethylene oxide and polymeric and non-organic compounds.

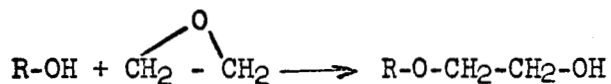
Ethylene oxide is a highly reactive agent capable of participating in a wide variety of reactions and capable of modifying the physical and chemical properties of many compounds. Two types of reactions are of particular interest in this program; condensation and polymerization. The condensation of ethylene oxide with another compound proceeds by attachment of the broken epoxy ring to an active hydrogen. Polymerization, catalyzed by bases and other inorganic salts, forms compounds of low volatility, potentially hazardous to electrical contact and thermal control surfaces.

INTRODUCTION

Ethylene oxide, alone or in conjunction with fluorocarbons such as Freon 12, has been used as an effective fungicide, fumigant and sterilization agent. It will kill bacteria, insects, fungi and other organisms. It has been particularly valuable in systems where heat sterilization is not practical. Chemically, ethylene oxide is very reactive and therefore not all materials can be sterilized with ethylene oxide without undergoing some chemical and physical change which may prove detrimental to the materials' function. Ethylene oxide has been committed, for use as a sterilant, for various spacecraft systems. It is important to be forewarned of any deleterious effects that ethylene oxide can produce and to compensate or redesign. Failure to do so could cause loss of a spacecraft because of malfunction of a component. Consequently, the literature has been searched from January 1962 to the present in order to gain insight into possible damage that can result from ethylene oxide treatment. Prior to January 1962 an extensive literature search had been made¹ so this literature search brings the survey up to date.

In searching the literature no direct reference has been found as to the damage of a material that is treated with ethylene oxide. However, through a knowledge of the reactions that polymers, organics and other materials can undergo with ethylene oxide, insight can be gained as to possible damage that can result.

Briefly, the high reactivity of ethylene oxide is due to the highly strained nature of a three membered oxirane ring. This ring structure can be easily opened and undergo condensation with itself or a second substance. Compounds which possess labile hydrogen are particularly reactive towards ethylene oxide. For example, alcohols can react as follows



Other hydroxy containing compounds which include such natural compounds such as cellulose in its various forms (starch, proteins, keratinous substances, lignin) can react with ethylene oxide. Thus, treatment of such materials with ethylene oxide can modify the chemical and physical properties.

Labile hydrogen can also come from other sources, such as carboxylic acid groups, inorganic acids (hydrochloric acid), thiols, amines, etc.

Ethylene oxide also undergoes condensation reactions very easily. Aldehydes and ketones can be induced to condense with ethylene oxide to form cyclic acetals or 1,3-dioxolanes.

Scarcely a polymer exists that does not have functional groups that are not potentially reactive with ethylene oxide. The following literature review is aimed at providing reaction parameters for ethylene oxide and materials and some of the products of such reactions.

LITERATURE REVIEW

Ethylene oxide as well as other 1,2-alkylene oxides have been used to prepare polyethers used in the preparation of polyurethanes in a one step reaction.² The polyether formation was catalyzed by using a base such as ammonia, piperazine or an amino compound of the general formula $H_2N(R-NH)_nR-NH_2$, where R may be the same or different aliphatic, aliphatic-aromatic, or cycloaliphatic hydrocarbon residues, and n is 0-5. An isocyanate such as 4,4'-diisocyanatodiphenylmethane was then reacted with the polyether to form a urethane.

Polyhydric alcohols such as $C(CH_2OH)_4$ have been treated with propylene oxide or ethylene oxide to give oxypropylated or oxyethylated compounds.³ These reactions are catalyzed by water and potassium hydroxide and take place at 100°C and moderate pressures (less than two atm.). The resulting compounds can be treated with polysiloxanes and diisocyanates to give polyurethane foams.

Branched tetrols have been prepared by the reaction of ethylene diamine successively with propylene oxide and ethylene oxide to give a molecular weight of 2500-3000.⁹ These tetrols have been reacted with 4,4'-diisocyanatodiphenylmethane and 1% by weight of dibutyltin dilaurate or stannous octanoate to yield flexible cellular material.

Polyhydroxy compounds prepared by saponification of the chlorine atoms in polyhydroxyethers derived from epichlorohydrin and ferric chloride as a catalyst have been reacted with organopoly-isocyanates to give polyurethanes of high quality¹⁰. A typical polyhydroxyether has been made by treating a mixture of tetrahydrofuran 36.5, epichlorohydrin 1, and ethylene oxide 7.5 with ferric chloride 0.2 and sulfonyl chloride 1.0 mole at 35-40°C. The chlorine exchange was then effected using a solution of sodium hydroxide in ethylene glycol.

Rigid or flexible foamed polymers have been prepared by the reaction of isocyanate-modified alkylene oxide addition products of tetramethylol-cyclohexanol (foaming agent) with polyisocyanate and water¹¹. The polyhydric alcohol is prepared by the reaction of 2,2,6,6-tetrakis (hydroxymethyl) cyclohexanol and propylene oxide.

Rigid polyester urethane foams have been made by adding a polyester (from trimethylpropane adipic acid and phthalic anhydride) to 2-ethylhexyl-ester of penta-sodium tripolyphosphate and ethylene oxide condensate with tert-octylphenylmethane¹². The ethylene oxide condensate was prepared by condensing ethylene oxide with tert-octylphenol in the presence of trioxane.

Polyurethane foams have been prepared from poly(oxypropylene)diol (mol. wt. n 2000 and prepared from propylene oxide and water), 2000 parts branched poly(oxypropylene oxide and glycerol), 0.25 part zinc dinnyl dithiophosphate, 3.2 parts alkylsilane-poly(oxypropylene) copolymer, and a solution of 1.75 parts 4-dimethylamino-pyridine in 11.6 parts water, 152 parts of a 80:20 tolylene 2,4- and 2,6-diisocyanate mixture was added, and the resulting mixture was placed in a mold. Expansion gave a flexible foam with good physical properties¹³.

Some of the polyethers prepared from ethylene oxide have found application as emulsifiers for latexes⁴. These emulsifiers are prepared by the reaction of 5-50 moles of ethylene oxide with 1 mole phenol or fatty alcohol.

It is interesting to note that ethylene oxide can polymerize in the presence of the appropriate inorganic catalyst. For example, the sulfates of calcium, zinc, barium, magnesium, and aluminum are such catalyst⁷. These salts with the exception of zinc sulfate yield solid polymers, the latter yields a liquid polymer. These polymerizations can even be carried out at atmospheric pressure and moderate temperature (180-200°C in the case of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The resulting polymers are soluble in benzene and water, but insoluble in petroleum ether and aliphatic hydrocarbons.

The ability of ethylene oxide to add the hydroxyethyl group to a compound results in increasing the water solubility of the compound. Hydrophobic materials such as fatty acid, fatty amines, fatty alcohols, alkylated phenols have been converted to polyoxyethylated derivatives which have found use as surface-active agents, dispersants, penetrants, detergents, stabilizers, emulsifiers and wetting agents.

Alkylphenol-formaldehyde and alkylcresolformaldehyde resins have been reacted with ethylene oxide to form nonionic surface-active products⁵. For example, nonionic surface-active products have been prepared by condensation of isooctylphenol-formaldehyde, dodecylphenolformaldehyde, isooctylcresol formaldehyde and dodecylcresol-formaldehyde with ethylene oxide. Sodium hydroxide is used as the catalyst to promote the reaction of ethylene oxide with these resins.

Non-ionic surface-active products have been prepared by the reaction of naphthenic acids and ethylene oxide using sodium hydroxide as a catalyst⁶.

Nylon has been made more soluble in ethanol by ethoxylation with ethylene oxide⁸. The resulting product is soluble to the extent of 10-40% in hot ethanol and can be deposited from such solutions at room temperature. The products are useful in the deposition of diffusion barriers in laminated non-metallic cells and bladders for fuels and lubricant transport, and for impregnating and sizing of porous and (or) fibrous materials, e.g., felt, paper and leather.

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Copolymers of ethylene oxide or propylene oxide with fluorinated monomers such as trifluorochloroethylene, perfluoropropene, 1,1-difluoro-2-chloroethylene, or perfluorobutadiene using ultraviolet radiation or a chemical catalyst such as ditert-butylperoxide yielded internally plasticized polymers¹⁴. These are useful for lubricants, elastomers, and protective coatings.

Polyethoxyamine prepared by the reaction of ethylene oxide and primary aliphatic tertiary C₁₈₋₂₄ amines have been used to plasticize resinous polycarbonates¹⁵:

Water soluble polyesters have been prepared by the reaction of unsaturated water soluble acidic polymers containing more than 10 COOH groups/mol. with water soluble polyethers containing more than 7 aliphatic ether linkages (preferably approximately 100)/mol. The soluble polyester is made insoluble by heating to 150-225°. The polyethers are prepared by treating ethylene or propylene oxide with hydroxy containing compounds such as alcohols, glycols, glycerol, phenol, natural glucosides or sugars, and their copolymers. Suitable acids are polyacrylic or methacrylic acids or copolymers of these with styrene vinyl chloride, vinyl toluene or isobutylene.

An interesting study was made of the competitive reaction of ethylene oxide in a mixture containing NH₂, NH and OH groups¹⁷. It was found that the hydroxyl group catalyzed the reaction of ethylene oxide with amines. The effect of the catalyzer was proportional to its amount and to the reaction temperature. The reaction took place preferentially with the amino group in the mixture. Finally when the reaction was carried out at 70-80°C with ROH as the catalyzer, colorless products were obtained.

The catalytic effect tertiary amines on the reaction rate of ethylene oxide with several saturated and unsaturated long chain alcohols was studied¹⁸. It was found that the reaction rate increased with the basicity of the amine, but the rate was affected by N-substituted groups. The reaction rate decreased with the chain length of the alcohol and the rate of unsaturated alcohols was more rapid than that of saturated alcohols of the same carbon number. The maximum rate was obtained at 80°C with any catalyst. The reaction rate increased rapidly with the molar ratio of catalysts to alcohols up to the ratio 0.3/1.0, but beyond the ratio 0.5/1.0 the rate became nearly constant. Finally, tertiary amines were more effective for the reaction of ethylene oxide with alcohols than potassium hydroxide as a catalyst at a low temperature (90-70°C).

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