ON THE ORGANIC SYNTHESIS RELATED TO THE SODIUM INDUSTRY I
ON THE SYNTHESIS OF POLYETHYLENEGLYCOLS

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INTRODUCTION

In the industry of manufacturing polyethyleneglycol, in addition to the optimum condition of manufacturing procedure, it is of great importance to produce the colourless or very white polyethyleneglycols for its wide uses. This study aimed at to get the optimum condition for its industrials manufacture and how to avoid the colouring on manufacturing without bleaching, for instance, by H_2O_2 etc.

SYNTHETIC REACTION OF POLYETHYLENEGLYCOLS

On Catalytic Reaction in the Polymerization Reaction

Bordered on a molecular weight some 1540*, as the catalysis, NaOH is generally used for the synthesis below M. W. 1540, but CH_3ONa is used above M. W. 1540. The author guesses that the very relation of the equilibrium

$$HONa + HO \cdot CH_2 - CH_2 \cdot OH \rightleftarrows HOH + NaO \cdot CH_2 - CH_2 \cdot OH \qquad (1)$$
            (or its polymer)

or
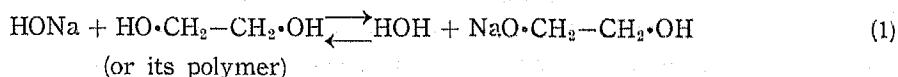
$$CH_2ONa + HO \cdot CH_2 - CH_2 \cdot OH \rightleftarrows CH_3OH + NaO \cdot CH_2 - CH_2 \cdot OH \qquad (2)$$
            (or its polymer)
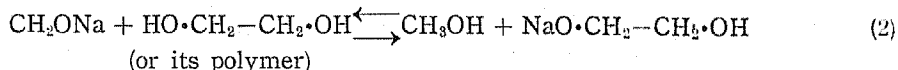
is the catalysis of polymerization reaction. NaOH or CH_3ONa in itself can not be expected as the catalysis, but they are no more than the staffs which supply the catalysis (1) or (2). Making on array in order to grow to the polymers by a very little Alkali, Na^+ ions must shift from polymer to polymer, and then for the benefit of activity of Na^+ ions there must be H_2O which gives the relation (1). It is certain for H_2O to back up the catalytic reaction, the same is true for CH_3OH or like matters too. This is the reason why the trace of H_2O is said to be the active catalyst for the polymerization. [1]

The CH_3ONa catalyst is helped by CH_3OH, in the same way as the NaOH

catalyst is done by H_2O. According to P. B. report, therefore, CH_3ONa in 10% methanol solution is added into oxydwachs, and after stirring, the methanol is driven out by vacuum. The author, however, conjectures that it perhaps cannot be thoroughly driven out. In order to expel the H_2O and CH_3OH out of the system, it will be required high vacuum and much time etc.[2] This is seen in the case of fractional precipitations too.

Different from the case of CH_3OH, when $NaOH$ and H_2O are used as catalyst, it is not necessary to add H_2O moreover, because even on the treatment with the vacuum distillation of glycol, the latter is so hygroscopic that it is difficult to remove H_2O from it perfectly. It is clear for glycol to hydrogene-bond from the view-point of its high boiling point. H_2O in glycol will be hold by the phenomenon of solvation. It is anologized from the fact that, even if glycol is distilled in vacum, there is a minute amount of aldehyde contained in it, which is tested easily from the reduction of Tollen's reagent. It is useful to remember the fact that, in the use of CH_3ONa as catalyst, vacuum is applied when methanol is driven out, but, as seen in P. B. report, it is not driven out even near the reaction temperature, therefore, a certain amount of methanol will remain in the oxydwachs which is got polymerization.

NaOH Catalyst at the Case below M. W. of about 1540

The reason why $NaOH$ is used as the catalyst of polymerization instead of CH_3ONa is perhaps the followings:

(1) The treatment of $NaOH$ is easier than CH_3ONa, the latter requires special preparation and care on using for its high hygroscopic nature.

(2) For the hygroscopic property of glycol, CH_3ONa is inclined to separate into CH_3OH and $NaOH$.

(3) When the reaction temp. is 130°C or higher, the more volatile methanol of lower boiling point than H_2O is inclined to driven out, and the catalytic condition of Eq. (2) becomes unsatisfactory, consequently the reaction will become longer. It is still more so when ethylene oxide is passed through the system before the polymerization in order to remove the cause of colouring or aldehyde in glycol.

(4) Generally alcohol, ROH, is polymerized to a long chain molecule with ethyleneoxide in alkaline solution. In the same way it is found that the alkaline methanol or CH_3ONa becomes $CH_3OCH_2CH_2ONa$ with ethyleneoxide, and so it is not desirable to use CH_3ONa as catalyst with CH_3OH on starting from glycol of low molecular weight.

After all, CH_3ONa is difficult to treat for the sake of its extraordinary hygroscopicity, for if it is used like the statement of P. B. report, CH_3ONa in methanol solution is added to the system, then it is necessary to drive out needless methanol by vacuum. On the other hand in the case of $NaOH$, its catalytic activity is given by the trace of H_2O already held in glycol, together with the H_2O produced in

the Eq. (1). They become a help for Na+ ions to move about in the system for growing of polyethyleneglycol in an array to long chains. The amount of H_2O yielded by equilibrium relation (1) will be insufficient for the polymerization reaction, and the trace H_2O already existed in glycol will participate in it.

CH_3ONa Catalyst at the Case above M. W. of about 1540

Methanol CH_3OH: Methanol is a polar organic solvent, it is close to ionic compound rather than non-polar compound, and its ability of solution is near somewhat to water than ethanol. Methanol is comparatively stable in Alkali, but it produces methylate with concentrated Alkali. Methylate is remarkably hygroscopic and the following reaction is reversible:

$$MaOCH_3 + H_2O \rightleftarrows NaOH + CH_3OH \text{ (reversible)}$$
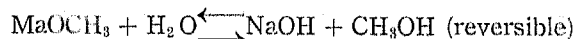
($NaOCH_3 + CH_3OH$) is colourless and very hygroscopic crystal. Sodium methylate has some electric conductivity[3] in methanol solution, and in this case the mobility of Methyl-ion has been measured[4].

From the above, the activity of Na+ in CH_3OH is anologized similar to Na+ ion in H_2O.

$$H_2O + CH_2 - CH_2 \longrightarrow HOCH_2 - CH_2OH, \qquad \Delta H = ca. -25 \text{ kcal./mol.}$$
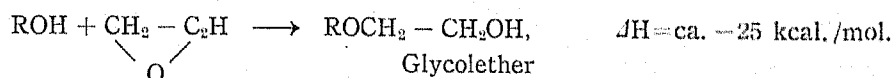$$\diagdown O \diagup \qquad\qquad \text{Glycol}$$

$$ROH + CH_2 - C_2H \longrightarrow ROCH_2 - CH_2OH, \qquad \Delta H = ca. -25 \text{ kcal./mol.}$$
$$\diagdown O \diagup \qquad\qquad \text{Glycolether}$$
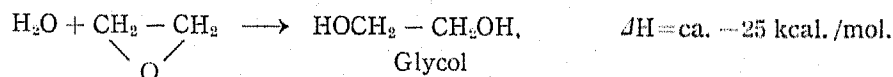
From these same values of ΔH[5], it will have something in common that such reactions like these are carried out generally near 130°C (similar to the case of phenols and naphthols). The reaction

$$CH_3OH + CH_2 - CH_2 \longrightarrow CH_3OCH_2 - CH_2OH$$
$$\diagdown O \diagup$$
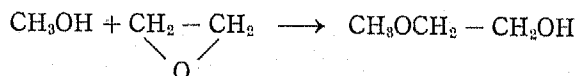
produces in general the compound of mono-molecular ether form by acid catalyst, moreover alcohols and phenols polymerize to long chain molecules or poly-molecular ether form with alkali catalyst.

Methylglycol: Molecular weight, 76; boiling point at 740mm Hg, 124°C; D_4^{20}, 0.967; evaporation time (ether=1), 34.5. If methylglycol is produced, it reacts with aldehyde in the system,

$$2CH_3OCH_2CH_2 + CH_3CHO \longrightarrow CH_3CH \cdot (OCH_2CH_2OCH_3)_2 + H_2O,$$
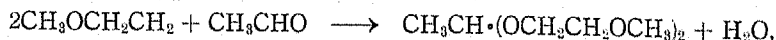
this is found by HCl acidic at 25°C.[6] This will perhaps occur with alkaline catalyst too, if HCl becomes acid-base catalyst in common with acid and alkaline mediums.

Industrial preparation of glycolether is performed by the method similar to the preparation of glycol and diglycol,[5] The end group of synthetized high polymer, which is —OH group, can easily methylate or acetylate. From these facts, it is

seen that the polymer, the end group of which is —CH_8 group, can be produced from CH_3ONa too. The molecular weight of polyoxyethylene analized from the end group method coincides well with that measured by the freezing point method.

$$HOCH_2OCH_2CH_2O\cdots\cdots CH_2OCH_2OH \ : \ \alpha\text{-polyoxymethylene}$$

$$(CH_3O) \ CH_2OCH_2CH_2O\cdots\cdots CH_2OCH_2(OCH_3) \ : \ \text{methyl compound}$$
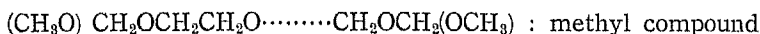
In a substance, its dielectric constant being ϵ, the work done, requiring to separate one valency positive and negative ions, electricities are $\pm e$, from a distance γ to ∞, is $e^2/\epsilon\gamma$. Different from the circumstances in a paraffin ($\epsilon=2$) or vacuum, CH_3ONa will tend to dissociate in the non-water solvent of methanol ($\epsilon=31.8$) into CH_3O^- and Na^+, similar to the dissociation of $NaOH$ into Na^+ and OH^- in H_2O ($\epsilon=80$). This is surmised from the fact that CH_3ONa has an electric conductivity, for electricity will be transported mainly by ions in this case. Thus methanol has large ϵ-value, hence the value $e^2/\epsilon\gamma$ becomes small; therefore, CH_8ONa will easily dissociate into CH_3O^- and Na^+ ions which will be solvated by CH_3OH in the system.

As getting above M. W. ca. 1540 and the number of oxyethylene groups increasing, polyethyleneglycol loses its solubility in H_2O little by little. Therefore, when in the system in which the equilibrium Eq. (1) acts as catalyst, the faculty of H_2O that gives the ability for Na^+ ion to travel from a molecule to a molecule becomes smaller, then methanol must take the place of H_2O which is lower soluble than the former as a polar organic solvent in connection with polyethyleneglycol, and being replaced $NaOH$ by CH_8ONa, equilibrium Eq. (2) becomes to act as catalyst.

One method to make use of CH_8ONa as Catalyst: According to P. B. report, on starting from oxydwachs, methanol solution of 10% CH_8ONa is added to it and stirred to mix well, in the next place methanol is eliminated under vacuum, moreover expelled out by passing N_2, and finally the contents are heated at 120°C.

This procedure requires a skilful treatment about the extraordinary hygroscopic nature of CH_3ONa, and applying this method it is convenient to save the procedure to remove the methanol which is used for preparation of CH_8ONa and protected the latter from the moisture in the air. Moreover from above treatment the surviving CH_3OH which cannot perfectly be removed out gives an activity to CH_8ONa as catalyst together with the methanol produced by equilibrium Eq. (2). It is believed that the trace CH_3OH will be needed for the polymerization starting from oxydwachs, on remembering that the trace H_2O is said to be a catalyst as to the formation of low molecular polymer. Too much methamol is not good, for it produces methyl cellosolve together with ethyleneoxide by alkali catalyst and this follows to grow to methylcarbitol[1]. $NaOH$ generally has a water of crystalization, and similarly $NaOCH_8$ makes a colourless and very hygroscopic crystal with CH_3OH.

From above consideration, it is clear that at lower molecule $NaOH$ is good for

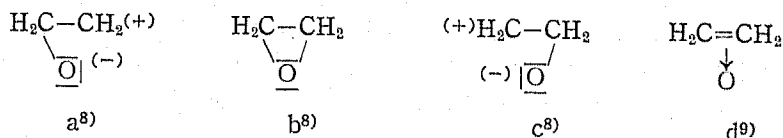polymerization catalyst, but for the preparation of the higher molecule CH_3ONa becomes suitable than NaOH. In fact the corresponding terms in the equilibrium Eq. (1) and (2) resemble respectively in nature. There are experimental facts that on using CH_3ONa as catalyst for polymerization of M. W. below 1540 or on using NaOH for M. W. above 1540, in both cases the distribution of molecular weight spreads more than the case of opposite using of catalysts. These facts could be understood by the property of catalysis as the equilibrium relation (1) and (2), for if CH_3ONa is used in the case of lower molecular weight, it is changed out combining with the bulk of water which is strongly retained by lower glycol to NaOH, and so

$$CH_3ONa + H_2O = CH_3OH + NaOH$$

the NaOH is difficult to act as catalysis by the equilibrium (1) on account of lacking sufficient H_2O, consequently Na^+ ion is hard to run about making active part of $-OCH_2CH_2O^-Na^+$; hence partial molecules only becomes apt to polymerize preferentially, that is, the distribution of molecular weight becomes wider. On the other hand, if NaOH is used for making the higher glycol the catalysis (1) is not so adequate as (2), for H_2O is so less familiar to higher glycol than CH_3OH that in this case the polymerization is not so smooth as in the case of catalyst CH_3ONa and only partial molecules tend to grow higher, that is, the distribution becomes wider. In fact from about M. W. 1540 higher the solubility of H_2O to polyglycol remarkably decreases (see later table). In the case of using NaOH as catalyst (0.26% of starting oxydwachs,) absorption velocit yof $C_2H_4 \cdot O$ into the system, after M. W. nearly 1540, is much less than in the case of CH_3ONa (1% of starting oxydwachs), hence in the former case the required molecular weight is not gained, namely beyond expectation the measured viscosity and the melting point are lower, moreover their ranges are broad (for the standard of the manufactured goods the quantity of Na used is restricted). According to P. B. report, for the production of M. W. 4000 CH_3ONa is the optimum catalyst, BF_3 gives only a polymer of lower molecularweight and it is said that Al $(OH)_3$ will probably polymerize $C_2H_4 \cdot O$ with explosion.

Reaction of Ethylene oxide

The active nature of ethyleneoxide is expressed as the following forms[1]:

$$
\begin{array}{cccc}
H_2C{-}CH_2^{(+)} & H_2C{-}CH_2 & {}^{(+)}H_2C{-}CH_2 & H_2C{=}CH_2 \\
\diagdown \underline{|O|}^{(-)} & \diagdown \underline{O} \diagup & {}^{(-)}|\underline{O}\diagup & \downarrow \\
 & & & O \\
a^{[8]} & b^{[8]} & c^{[8]} & d^{[9]}
\end{array}
$$

In "d" form a π electron bond is conceived, that is, it is supposed that oxygene atom is bound to ethylene by means of donor–acceptor bond utilizing electron in the double bond. [9]

$$C{-}O{-}C \qquad \text{bond angle } 61° \ 41'$$
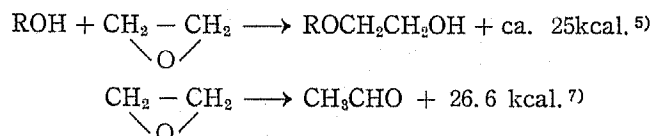
O–C–C　　bond angle 59° 9′

$C_2H_4 \cdot O$ shows neutrality for litmus, but it has basic in the meaning that it forms oxonium salt with mineral acid anhydride, and this is the general nature of most acyclic ethers. An advanced explanation about this basicity is given by the fact that $C_2H_4 \cdot O$ produces with different metalic salts, for instance, $MgCl_2$, ethylenechlorhydrine and corresponding metalic hydroxide:

$$2CH_2-CH_2 + 2H_2O + MgCl_2 \longrightarrow 2CH_2Cl \cdot CH_2OH + Mg(OH)_2$$

Most reactions of $C_2H_4 \cdot O$ consist in the unfolding of 3-membered ring; among a few exception there are the above mentioned formation of oxonium salts and further probably the formation of like a compound $(C_2H_4 \cdot O)_2Br_2$. Chemically high activity of $C_2H_4 \cdot O$ is comparable to the behaviour like the two membered system $-C=C-$, as understood from above form "d". The ordinary explanation about the reaction nature of $C_2H_4 \cdot O$ is originated in a theory of tensioned strain proposed by Buyer. This theory states that the stress or tension within $C_2H_4 \cdot O$, which causes the values of bond angles biassed from those in most ordinary aliphatic compound, gives the characteristic for its chemical activity. Of course if such a stress or strain is symmetry about the center of molecule, it will increase its stability on a certain occasion, but since the limiting form of mesomeric has not such a porticular symmetry, it is natural to be prone to react with approaching molecule. In the course of wavering among the above-mentioned "a", "b", "c", and "d" forms, acquiring the necessary activated energy, the distance between C and O grows shorten, and at the same time a proton moves resulting in that the molecule shifts to acetaldehyde, the more stabilizing form in energy, emitting a free energy of 23.3 kcal. (under certain investigators, 30.4 or 33.4 kcal). If this new acetaldehyde takes this emitting energy upon itself, for the sake of its own possessing heat energy it goes on to decompose into CO and CH_4 with activating not yet reacting molecules in accordance with the Christiansen Kramers' hypothesis.

$$CH_3CHO \text{ (Gas)} \longrightarrow CO + CH_4 + 2.3 \text{ kcal./mole}[7]$$
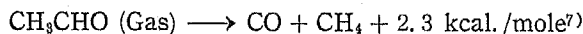
If before leaving from the reacting system, the new aldehyde reacts with $C_2H_4 \cdot O$, producing coloured aldehyde resin, that is, the polyethyleneglycol colours. The reaction:

$$ROH + CH_2 - CH_2 \longrightarrow ROCH_2CH_2OH + ca. \ 25kcal.[5]$$
$$\diagdown O \diagup$$

$$CH_2 - CH_2 \longrightarrow CH_3CHO + 26.6 \text{ kcal.}[7]$$
$$\diagdown O \diagup$$

shows that the heat of reaction to the addition polymerization of $C_2H_4 \cdot O$, $22[10]$–25 kcal., is not largely different from that to the energy of isomerism, 26.6–33.4 kcal.[11] Therefore, the temperature necessary to activate the reaction of $C_2H_4 \cdot O$ is

that at which the isomerism will occur. According to some investigators the heat
of isomerism is said to be about 24 kcal./mole. In view of these facts, in order to
make addition polymerization of $C_2H_4 \cdot O$, it will be sure to accompany the colouring
product due to the production of aldehyde resin.

Therefore it is necessary to devise for aldehyde not to remain in the system,
not to contact with alkali if possible, and the reaction temperature must not be
raised over a certain point at every place in that system. Summing up so far the
empirical facts, the optimum reaction temperature is about 125–130°C. If the reac-
tion temperature is too high, in addition to the fact that the isomerism get predo-
minant, some depolymerization becomes remarkable. By the way the heat of
formation of $C_2H_4 \cdot O$ is said to be 17.7 kcal./mole. [11, 13]

Reaction of Ethyleneoxide in a acidic aqueous Solution: As above the bond angle
in CH_2-CH_2 fairly strains from regular value, accordingly it is easy to open its
$\diagdown O \diagup$

ring, and $C_2H_4 \cdot O$ is extremely active in its reaction. It is generally understood that
glycol is produced as the result of following reaction,

$$CH_2-CH_2 + H_2O \longrightarrow HOCH_2CH_2OH, \qquad \Delta H = ca. \ -25kcal./mol. \qquad (3)$$
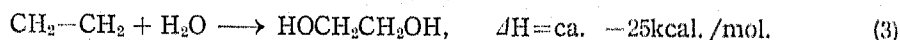
It is, however, not simple in acidic aqueous solution as such a reaction. [14] Both the
simple reaction with H_2O as the above and the catalytic reaction with oxonium ion
coexist. By perchloric acid catalyst, the reaction velocity v is

$$v = [C_2H_4 \cdot O] \{k_1 + k_2 [CH_3^+]\} \qquad (4)$$

Besides this, as a negative ion from the acid takes part in the reaction on such an
aqueous solution including halogeno–hydrogenic acid or carbonic acid, in addition to
the above two reactions, the following Eqs. (5) and (6) participate in the reaction.

$$CH_2 - CH_2 + Cl^- + H_2O \longrightarrow CH_2Cl + OH^- \qquad (5)$$
$$\diagdown O \diagup \qquad\qquad\qquad CH_2OH$$

$$CH_2 - CH_2 + Cl^- + H_3O^+ \longrightarrow CH_2Cl + H_2O \qquad (6)$$
$$\diagdown O \diagup \qquad\qquad\qquad CH_2OH$$
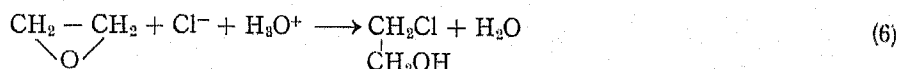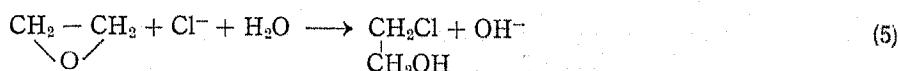
Eq. (5) is independent of oxonium ion, but Eq. (6) depends the latter, hence the entire
reaction velocity v becomes

$$v + (C_2H_4 \cdot O) \{k_1 + k_2 [OH_3^+] + k_3 [Cl^-] + k_4 [Cl^-] [OH_3^+] \qquad (7)$$
k_1, k_2 are related to glycol production.
k_3, k_4　　　 // 　　 chlorhydrine production.

They say as a result of Eq. (5), the ratio of the velocity with which KCl and HCl
consume $C_2H_4 \cdot O$ is 1:50, but if not so the velocity ratio becomes equal to the ratio
of oxonium ion, namely $1:10^6$. [6]

Utilizing the contraction of volume, BRÖNSTED et al. seeked for the velocity v

of Eq. (3) by means of dilatometer. There was a relation:

$$\frac{k_1}{k_2} = \frac{k_3}{k_4}$$

This explanation was done as follows:

$$\begin{matrix} CH_2 - CH_2 + H_2O & k_1 & CH_2OH + OH^- \\ \diagdown O \diagup \quad\quad H_2O & \longrightarrow & CH_2OH \quad H^+ \end{matrix} \tag{8}$$

$$\begin{matrix} CH_2 - CH_2 + H_3O^+ & k_2 & CH_2OH + H_2O \\ \diagdown O \diagup \quad\quad H_2O & \longrightarrow & CH_2OH \quad H^+ \end{matrix} \tag{9}$$

In Eq. (8), a proton is taken away from the upper H_2O and OH^- ion is carried off from the lower H_2O. In Eq. (9), the upper side turns into an oxonium ion from which a proton is carried off and OH^- ion is taken away from the lower H_2O as well. In the next place,

$$\begin{matrix} CH_2 - CH_2 + H_2O & k_3 & CH_2OH + OH^- \\ \diagdown O \diagup \quad\quad Cl^- & \longrightarrow & CH_2OH \end{matrix} \tag{10}$$

$$\begin{matrix} CH_2 - CH_2 + H_3O^+ & k_4 & CH_2OH + H_2O \\ \diagdown O \diagup \quad\quad Cl^- & \longrightarrow & CH_2OH \end{matrix} \tag{11}$$

Eqs. (10) and (11) are not different from Eqs. (8) and (9) merely except that the lower H_2O is supplanted by Cl^- ion, hence

$$\frac{k_1}{k_2} = \frac{k_3}{k_4}$$

comparing Eqs. (8) and (9) with Eqs. (10) and (11), H_3O^+, of course, is stronger acid than H_2O, the former is more liable to release a proton than the latter, therefore,

$$k_2 > k_1 \quad\quad\quad\quad k_4 > k_3$$

This reaction is the typical example in which both positive and negative reagents attack the carbon atoms simultaneously.

Several Kinds of Catalysts and the Reactions between Ethylenoxide and various Matters

Catalysts: There are NaOH, KOH, ZnO, Al_2O_3, PbO, $ZnCl_2$, $SnCl_2$, hydrosilicates (bleaching earth) as well as Mg, Al, Fe etc.

Reaction of $C_2H_4 \cdot O$ with various Matters: It is necessary to know the reaction properties of ethyleneoxide for precaution on treatment. According to P. B. report[7] an outline of the reaction properties of $C_2H_4 \cdot O$ is as follows:

1) Metals

(1. 1) **K:** In a beaker pure or industrial liquid $C_2H_4 \cdot O$ and K react with explosion. In sealed tube, however, an explosion occurs merely with pure $C_2H_4 \cdot O$ and fine-grains of K carefully released from xylene adhered to its surface, but xylene previously added to $C_2H_4 \cdot O$ does not hinder the explosive reaction. 1% CH_3CHO content largely relaxes the explosive reaction, namely the explosion occurred after 10-20 minutes is prolonged to that after 10-20 hours.

(1. 2) **Na:** Even when $C_2H_4 \cdot O$ is heated with Na in sealed flask, the explosion does not occur as in the case of K. According to the peport of MAAS and BORNER, if Na contacts with $C_2H_4 \cdot O$ for a long time, the surface of Na changes and the vapour pressure of $C_2H_4 \cdot O$ somewhat rises.

(1. 3) **Other Metals:** When $C_2H_4 \cdot O$ is passed on a surface of activated reduced iron or such Ni, it seems to produce ethylene a little at 150°C, some more at 200°C. When Mg, Al, Zn, Fe, Ni, Cu, Brass, Hg, Pb and Sn are heated at 95°C together with $C_2H_4 \cdot O$ in sealed tube, violent reactions are not found. Such catalysts as igniting iron, igniting nickel, activated reduced iron and activated reduced nickel do not give violent reaction in sealed tube even at 95°C. The behavior such as the explosion of a sealed tube which contains K and $C_2H_4 \cdot O$, and the formation of oxidized film layer on Mg which is heated for a long time at 95°C with $C_2H_4 \cdot O$, are the effect for the metalic surface to form metalic oxides and ethylene (or this polymer) by $C_2H_4 \cdot O$. These reactions which are needed for storing an energy of 43 kcal. /mole. to deprive $C_2H_4 \cdot O$ of oxygen atom, are far more difficult than the oxidation of metals by oxygen in the air. In most cases when heated for seven days, besides the formation of metalic oxides it is found that some partial polymerization occurs. On the Al powder refined by sublimation, there is a little polymerization, and polymerization is hardly found with powdered copper (namely, when heated $C_2H_4 \cdot O$ with 5% Cu powder for 6–7 days at 95–98°C in a sealed tube, it is such extent as the polymerizatnio below 5% can be estimated). Iron of several forms indicates to be effective to polymerization on the whole. Brass (40% Zn, 60% Cu), Mg, and Ni take only little change with $C_2H_4 \cdot O$.

2) Chloride Anhydrides

Among metal chlorides, anhydrides of $AlCl_3$, $SnCl_4$, and $TiCl_4$ react violently even at −60°C, and iron chloride anhydride also shows atrong reactivity.

The mechanism of these reactions is conjectured as follows: like the polymerization of oleffines, the polymerization, in which electron acceptor reagents (such as $SnCl_4$ and $ZnCl_2$) act as catalysts, start from binding the carbo–cation produced by the addition of oxygen to these reagents with new oxygen of $C_2H_4 \cdot O$, being repeated the same reaction one after another.
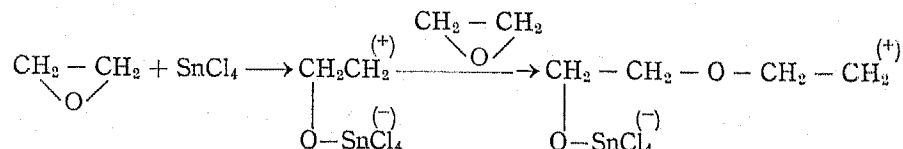
(2. 1) **AlCl₃;** $C_2H_4 \cdot O$ vapour burns on $AlCl_3$ powder but does not on granular one. Being added to $C_2H_4 \cdot O$, Al powder produces a violent reaction, but this reaction is regulated by dilution of inactive diluent as benzene. If $AlCl_3$ is not added by powder but added by large grains, the combustion does not occur, and the resulting decom-

position of grains can be regulated by cooling.

(2. 2) **FeCl₃ Anhydride**: This reacts vigorously but somewhat milder than the case of AlCl₃. During an experiment the liquid becomes brown (formation of iron oxychloride), and besides higher chloride polymer, ethylene chloride is found in the reaction products, but not acetaldehyde.

(2. 3) **SnCl₄**: This reacts violently with $C_2H_4 \cdot O$ even at $-60°C$, but combustion and flash are not found. It produces brown or dark brown resin product.

(2. 4) **TiCl₄**: Similar to SnCl₄.

(2. 5) **PCl₅**: This reacts together with heat and sound, and hence the reaction can be sufficiently regulated by cooling. Ethylene chloride is produced with higher chloride polymer products.

(2. 6) **POCl₃**: This scarcely reacts at $0°C$, but produces a little brownish liquid in sealed tube at $100°C$.

(2. 7) **PCl₃**: Similar to POCl₃, this produces a colourless liquid which has a stench like cacodyl.

(2. 8) **Phosgene**: Phosgene cannot affect pure $C_2H_4 \cdot O$ by itself at ordinary temperature in a beaker. It adds to the materials like $C_2H_4 \cdot O$ type together with tertiary bases.

(2. 9) **SnCl₂ and ZnCl₂**: When heated for seven days at $59°C$ these produce yellow wax without violent reaction. According to a reference[15], it is reported that $C_2H_4 \cdot O$ produces a crystaline polymer (m. p. $56°C$) being catalyzed for a long time with a little ZnCl₂ or Alkali. Let, however, $C_2H_4 \cdot O$ be alone in a sealed tube for one year, it becomes white solid (is it due to the Alkali from glass wall?), moreover this is accelerated by ZnCl₂ or Alkali.

(2. 10) **CuCl and CuCl₂**: Reaction is not found at room temperature. When heated in a sealed tube for sevendays at $95°C$, a little oily brown matter is produced.

(2. 11) **Other Metal Chloride Anhydrides**: HgCl₂, HgCl, CaCl₂, NaCl and KCl do not cause the reaction at ordinary temperature. According to ROITNER [16] crystaline CaCl₂ and $C_2H_4 \cdot O$ produce quantitative amount of ethylene chlorhydrine and Chalk (in the case of mild heating in sealed tube). BF₃ does not react in a short time by contact at $13°C$.

3) **Hydrated Metal Chloride**

These or crystal Al or hydrated iron chloride is not found to react violently. When $C_2H_4 \cdot O$ is heated with hydrated FeCl₃ for many days in a sealed tube, it results in the production of reddish brown solid, the colour of which is probably due to iron salt. Reacting with the chlorides of Mg, Fe, and Cu in the coexistence of H_2O, $C_2H_4 \cdot O$ produces glycol chlorhydrine and metal oxide. There is no report about a violent reaction. [17,18]
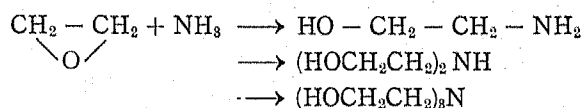
4) **Amines**

$C_2H_4 \cdot O$ does not react with ammonia or amines at ordinary temperature and

Table 1 Summary of Data

Metal chlorides	Heat of reaction per kg. $C_2H_4 \cdot O$ liquid	Reaction state
$AlCl_3$	-680 kcal	Very violent flash
$SnCl_4$	371	Violent
$TiCl_4$	Unknown	//
$FeCl_3$	252	//
$MgCl_2$	89	Undetermined
$ZnCl_2$	-27	Not violent, polymerizes mildy
$SnCl_2$	-49	//
$CuCl_2$	-79	//
$FeCl_3aq$	-228	Heat evolved such an extent not to recognize, a little polymerization
$CuCl$	-316	Not violent, very little polymerization
$HgCl_2$	-489	Not react
$CaCl_2$	-623	//
$HgCl$	-668	//
$NaCl$	-1900	//
KCl	-2507	//

dry state, but reacts very slowly at high temperature. In the coexistence of H_2O, changes to alkanol derivatives

$$CH_2 - CH_2 + NH_3 \longrightarrow HO - CH_2 - CH_2 - NH_2$$
$$\diagdown O \diagup \qquad \longrightarrow (HOCH_2CH_2)_2 NH$$
$$\longrightarrow (HOCH_2CH_2)_3 N$$

can explosively occur. [17] Piperidine yields oxyethylpiperidine with $C_2H_4 \cdot O$ at 100°C, [18] and piridine produces brown resin. [16] According to an experiment in sealed tube at room temperature, pure $C_2H_4 \cdot O$ does not react with 1% butyl amine, dibutyl amine or pyridine to such an extent to be able to recognize. [16]

Therefore, violent reactions between $C_2H_4 \cdot O$ and amines are probably due to the reaction in which N-oxyethylated compounds are formed along with a great quantity of heat emitted. On heating $C_2H_4 \cdot O$ with 5% base (which can accept the proton), a violent reaction is found.

5) **Bleaching Earth**

Certain kinds of these give violent reactions under certain conditions, accompanying always the typical stench of acetaldehyde or its polymers. It is under these circumstances only that the isomerization of $C_2H_4 \cdot O$ to acetaldehyde is found to occur certainly. (Other all violent reactions observed were that which were primarily the chemical reaction between $C_2H_4 \cdot O$ and its addition polymers.)

6) **Acids**

Among these, the addition of H_2SO_4 can only give a violent reaction, and this is not found in the case of HCl, HCOOH, oxalic acid, benzoic acid, and phthalic

acid anyhow at ordinary temperature.

7) **Peroxides**

30% H_2O_2 aqueous solution, benzoyl peroxide, sodium perboric acid and lead peroxide do not give any kind of reaction at ordinary temperature.

PROPERTIES OF GLYCOL

Ethyleneglycol is soluble in H_2O, but as increasing its molecular weight it becomes difficult to dissolve in H_2O. The center of its chemical reactivity exists in the hydroxyl radical at the both ends.

Three Characteristic Reactions of −OH Group

(1) **Acylation**: Ordinary acylating reagents are pyridine, acetic anhydride, acetyl chloride and phthalic anhydride.

(2) **Oxydation**: Oxydizing reagents are periodic acid, lead tetra acetate, potassium dichromate and potassium permanganate.

(3) **Reduction**
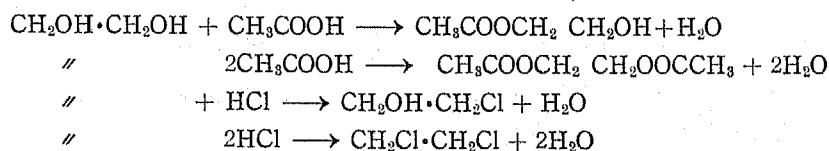
Quantitatively Reacting Reagents

Reagents consisted of hydroiodic acid, ammonium hexanitratocerate, silicotungstic acid and triphenyemethyl chloride and pyridine.

For quantitative analysis of industrial glycols many physical methods are used because of the interference due to −OH or $−NH_2=NH$ groups.

Reaction of Glycols

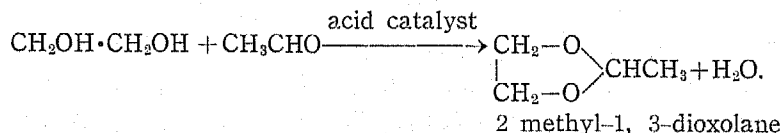Glycols are easily esterificated by organic as well as inorganic acids, acid halides and acid anhydrides.
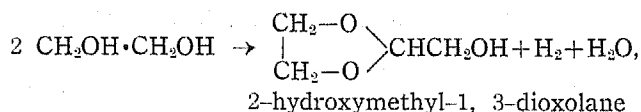
Reaction with Monobasic Acid:

$$CH_2OH \cdot CH_2OH + CH_3COOH \longrightarrow CH_3COOCH_2 \ CH_2OH + H_2O$$
$$\text{\textit{''}} \qquad 2CH_3COOH \longrightarrow CH_3COOCH_2 \ CH_2OOCCH_3 + 2H_2O$$
$$\text{\textit{''}} \qquad + HCl \longrightarrow CH_2OH \cdot CH_2Cl + H_2O$$
$$\text{\textit{''}} \qquad 2HCl \longrightarrow CH_2Cl \cdot CH_2Cl + 2H_2O$$

Reaction with Dibasic Acid: by this reaction glycols form cyclic or linear polyesters,

$$CH_2OH \cdot CH_2OH + HOOCRCOOH \longrightarrow [−O−CH_2CH_2−OOCRCO−]_n + 2H_2O.$$
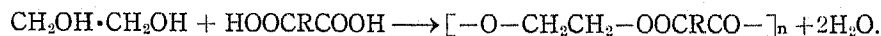
1, 2-glycol produces dioxolanes together with ketones or aldehydes,

$$CH_2OH \cdot CH_2OH + CH_3CHO \xrightarrow{\text{acid catalyst}} \begin{matrix} CH_2-O \\ | \qquad \ \ \rangle CHCH_3 + H_2O. \\ CH_2-O \end{matrix}$$

2 methyl-1, 3-dioxolane

Glycol can be dehydrated,

$$2 \ CH_2OH \cdot CH_2OH \rightarrow \begin{matrix} CH_2-O \\ | \qquad \ \ \rangle CHCH_2OH + H_2 + H_2O, \\ CH_2-O \end{matrix}$$

2-hydroxymethyl-1, 3-dioxolane

This is carried out on a supported copper-cromium catalyst at $200\sim350°C$.

Glycol can receive respective oxidation corresponding to the characteristic of catalyst and reaction condition. By contacting gas phase oxidation glycol produces corresponding dicarbonyl compound with high yield.

$$CH_2OH\cdot CH_2OH+O_2 \xrightarrow[\text{Cu catalyst}]{\text{gas phase}} \underset{\text{Glyoxal}}{CHO\cdot CHO}+2H_2O$$
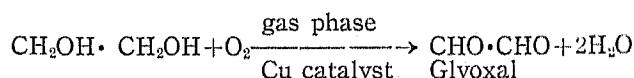
This aldehyde glyoxal is the most important material as the oxydation product of glycol.

By other oxydation method ethyleneglycol is oxidized to acetaldehyde, glyoxal, formaldehyde, glycolic acid and oxalic acid.

Density is the most convenient and plain nature of ethyleneglycol, hence it can be used as a measure of its purity. They say that the result of GIBSON and LOEFFLER[62] is the most reliable one. It seems that the lower values appeared in the other literature are due to the fact that the H_2O in glycol is not completely removed by purification or for the sake of absorption of moisture the value is probably lowered in the course of the measurement on account of the hygroscopic nature of glycol.

GIBSON & LOEFFLER[63] derived the following expression from their experiment by the method of least mean square,
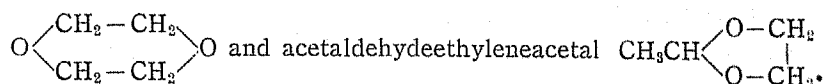
$$V=0.924848+6.2796\times10^{-4}(t-65)+9.2444\times10^{-7}\times(t-65)+3.057\times10^{-9}(t-65)$$

$V=$ Specific volume ml./g. $t=$ temperature °C

The value computed from this, deviates below 0.001% from the experimental values from 25°C to 105°C (see later Table).


PROPERTIES OF ETHYLENEOXIDE

When $C_2H_4\cdot O$ is distilled with a few quantity of H_2SO_4 or $ZnCl_2$, it produces acetaldehyde, diethylenedioxide

$$O{\Large\langle}\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}{\Large\rangle}O \text{ and acetaldehydeethyleneacetal } CH_3CH{\Large\langle}\begin{matrix}O-CH_2\\|\\O-CH_2\end{matrix}.$$

$C_2H_4\cdot O$ reduces silver nitrate solution. When aqueous solution of $C_2H_4\cdot O$ is treated with sodium amalgam, ethanol is produced. If $C_2H_4\cdot O$ is put in a pressure-proof sealed tube with H_2O and heated on a water bath, then it produces glycol and polyethyleneglycol. Affected by gaseous hydrogen chloride or cold hydrochloric acid, $C_2H_4\cdot O$ produces glycol chlorhydrine. $C_2H_4\cdot O$ produces chiefly glycol through hydrofluoric acid. Dry $C_2H_4\cdot O$ does not react with dry ammonia at 0°C under moderate pressure. Reacting with PCl_5, $C_2H_4\cdot O$ becomes ethylenchloride. Wet $C_2H_4\cdot O$ reacts with $CaCl_2$ and $Ca(OH)_2$, forming glycolchlorhydrine. $C_2H_4\cdot O$ reacts with cellosolve and produces carbitol. When $C_2H_4\cdot O$ reacts with glacial acetic acid and acetic

acid anhydride, it produces acetate of glycol and that of polyethyleneglycol. When passed on a nickel of 125-150°C in atomosphere of hydrogen, $C_2H_4 \cdot O$ produces acetaldehyde, crotonaldehyde and other products. Liquid $C_2H_4 \cdot O$ slowly polymerizes with pyridine. With chlorine as well as fluorine, $C_2H_4 \cdot O$ produces addition compound, for instance, 30% (weight) $C_2H_4 \cdot O$ and 70% chlorine react explosively at 0°C. When $C_2H_4 \cdot O$ allows to react with neutral H_2O, it only annexes so slowly that it decreases half an amount after 23 days. Reacting easily with excess C_2H_5OH, $C_2H_4 \cdot O$ produces $C_2H_5OCH_2 \cdot CH_2OH$.

The reaction

$$H_2C - CH_2 + H_2O \longrightarrow HOH_2C \cdot CH_2OH$$
$$\diagdown O \diagup$$
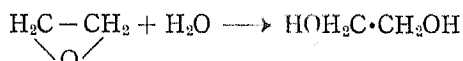
and the production of polyglycol are carried out in the neutral and alkaline pH as well as acid pH. $C_2H_4 \cdot O$ has a property to form much lower glycol in the acid medium than in the alkaline medium. At 0.1% acid concentration and ca. 60-70°C, the reaction velocity is already sufficient. Usually H_2SO_4 and oxalic acid are used as the acid, for these are apt to give a salt of low solubility, hence it is easy to draw out the product from the reaction system. Avoiding damage of vessels, in order to yield glycol at neutrality with sufficient reaction velocity, the process is carried out at 160-200°C and 10-20 atm. The process emitts heat, hence the system is strongly cooled or diluted with diluent. For the sake of no formation of diglycol $C_2H_4 \cdot O$ is used less than one fifth of H_2O.
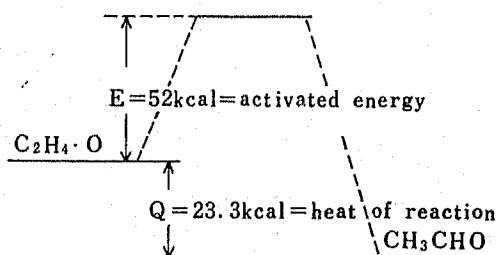
E = 52kcal = activated energy

$C_2H_4 \cdot O$

Q = 23.3kcal = heat of reaction
CH_3CHO

Fig. 1

Isomerization occurs in the relation of heat like the above figure. [19] This heat of isomerization. is near that of polymerization i. e. 22 kcal. It is confirmed that the decomposition of CH_3CHO and $C_2H_4 \cdot O$ strongly resembles with each other. By the way the heat of isomerization and the heat of reaction[20] described in P. B. report No. 1311 are somewhat different from above value (already mentioned), (see also later Table).

Polymerization and Depolymerization of Ethyleneoxide

It seems that it is difficult to make high degree of polymerization with glycolate as catalyst in place of NaOH or CH_3ONa. The explanation of this import confirms

the fact that the equilibrium relations (1) and (2) are true form of catalysis in the polymerization of ethyleneoxide. On growing to high polymer, decreasing hygroscopicity and the water being absorbed in glycol becomes probably little, hence equilibrium (1) is hardly settled for catalizing, namely in the case of high polymer, H_2O can not contract intimacy with polymer and it is difficult to hold the equilibruim (1) smoothly. Therefore, it is probable that the anew added glycolate only takes part in polymerization. When that glycolate only polymerizes taking a proper balance of heat, it is probable that the other high polymer not to any more polymerize in the system will depolymerize in that severe condition of reaction and moreover the permeation of $C_2H_4 \cdot O$ into the system will be difficult.

There are reports in which the polymerization were performed in H_2O or aqueous solution of glycol by H_2SO_4[21] and alkali[22] catalysts. Along with increasing of addition quantity of Alkali Catalyst, it is sufficient even to be at lower temperature and, when polymerized in autocrave, the pressure produced during the reaction becomes less quantity, moreover the reaction time grows shorter. As the result of study on the catalytic action of amines[23], it is confirmed that the magnitude of dissociation constant in water is well-matched that of catalytic action, hence agrees with the strength of basicity.

Matters	Dielectric const.	Temp. measured	Matters	Dipolemoment
Water	81[24]	19°C	Acetaldehyde	2, 69
Glycol	41, 2[26]	—	Glycol	2, 25
Methanol	31, 8	19°C	Water	1, 94 ± 0, 06
Ethanol	25, 8[25]	20°C	Ethyleneoxide	1, 88
			Methanol	1, 69
			Ethanol	1, 67

It is analogized that NaOH can dissociate in glycol from the fact that NH_3 will do in glycol as the followings :

dissociation const. of NH_3 in 99. 8% ethanol $0. 96 \times 10^{-7}$ [25]

　　　〃　　　　　　　　　　in water　　　　$1. 77 \times 10^{-5}$

In view of ε-value the dissociation constant of NH_3 in glycol will be a middle value between those of ethanol and water;

$1. 77 \times 10^{-5} >$ the value of NH_3 in glycol $> 0. 96 \times 10^{-7}$.

Namely from this fact it is clear that NH_3 in glycol will dissociate, further, of course, NaOH which is more basic than NH_3 will probably dissociate in glycol. As to the strength of catalytic action, NaOH is most strong and it grows weaker in order of triethylamine, ammonia, pyridine, dimethyl-aniline[23]. In Alkali catalyst the yield will be lowered than in the case of amines.

The reason why the equilibrium (1) can continue to act as catalysis, is grasped

by the fact[23] that the production of glycol by the reaction of H_2O and $C_2H_4 \cdot O$ along with the catalyst of Amines or Alkali, is remarkably suppressed in the glycol–water–ethyleneoxide system. Therefore the H_2O which participates in the equilibrium relation (1) will continue to exist in the system for a long time, and it is reasonable to add anew at every stage (glycol $\longrightarrow$ M. W. 300 $\longrightarrow$ M. W. 1540 $\longrightarrow$ M. W. 4000). In the case of CH_3OH, yielded methylglycol might present the catalysis like the equilibrium relation (2) instead of CH_3OH.

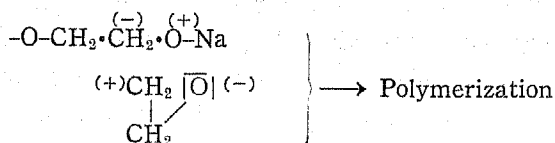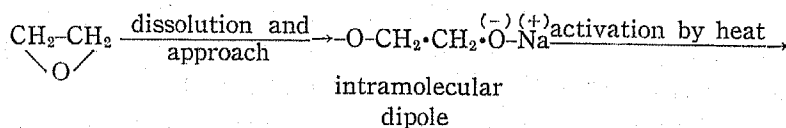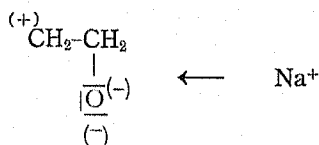If there is acetaldehyde in the system, the following reaction may also occur :

$$2CH_2OCH_2CH_2 \cdot OH + CH_3CHO \rightleftarrows CH_3 (O \cdot CH_2(H_2 \cdot OCH_3)_2 + H_2O \; \text{(reversible)}$$
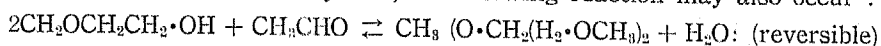
this reaction can occur in HCl acidic solution at 25°C.

According to the fundamental principle of Highfield, a polar matter has a tendency to dissolve in a polar solvent and a non–polar matter does so in a non–polar solvent. Such being the case, for the sake of the dissolution of $C_2H_4 \cdot O$, this and the part of glycol ($-O-CH_2-CH_2-O^--Na^+$) will probably intend to match their polarization along with the acceleration by means of the polar catalyst, and hence the dissolution of $C_2H_4 \cdot O$ in glycol or higher glycol results in the polymerization reaction by polar catalyst.

(polorization of $C_2H_4 \cdot O$)   (approach of ion)

$$\overset{(+)}{CH_2}-CH_2$$
$$|$$
$$\underline{|O}^{(-)} \quad \longleftarrow \quad Na^+$$
$$(^-)$$

$$CH_2-CH_2 \xrightarrow[\text{approach}]{\text{dissolution and}} -O-CH_2 \cdot CH_2 \cdot \overset{(-)}{O}-\overset{(+)}{Na} \xrightarrow{\text{activation by heat}}$$
$$\diagdown O \diagup$$
intramolecular
dipole

$$-O-CH_2 \cdot \overset{(-)}{CH_2} \cdot \overset{(+)}{O}-Na$$
$$\overset{(+)}{CH_2} \; \overline{|O|}^{(-)} \quad \Big\} \longrightarrow \text{Polymerization}$$
$$|\diagup$$
$$CH_2$$

Polarization by inductive effect and mesomery

As above illustration the polymerization occurs step by step. They say that the polymerization probably not to occur between higher polymers, for it appears to need at least an energy of 95 kcal. for breaking, such as the separation of H atom from a monomer and cutting–off of the –C–C– bond, and for yielding a free radical; hence it is not probably reached even by the heat of polymerization of ca. 25 kcal. to supply.

The author will mention a similar example in which this mechanism is to be approved. Ziegler et al. have studied in detail the polymerization of butadiene and its derivatives (moreover vinyl compound as styrene) promoted by Alkali metals. In order to grasp the intermediates, they used a large quantity of Alkali metal, further in some case experimented in a very diluted state. Then they could proove the fact that in the first place the 1-4-appendage (I) produces, going to drag a next butadiene molecule into the Na and carbon atoms of (I) by means of metalorganic synthesis, when it produces (II). By the way the heat of polymerization of butadiene is 500 kcal./kg.[7]

(I) $\overset{1}{Na-CH_2} \overset{}{CH} = \overset{3}{CH-} \overset{4}{CH_2-Na}$

(II) $Na-CH_2-CH = CH-CH_2-CH_2-CH = CH-CH_2-Na$
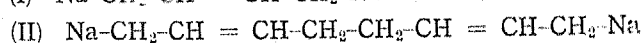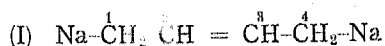
Performing the same experiments in Alkylated Alkali and Arylated Alkali, the intermediate like $R-CH_2-CH = CH-CH_2-A$ was found. In compliance with the form, the quantity and the way how to add concerning on the catalyst, the magnitude, and the direction of the reaction velocity are greatly influenced. Therefore the reaction product is remarkably changed in accordance with the fact that the catalyst is made to be porous or used greater quantity than that usually used, or that the reaction temperature is raised. Polymerization occurs sometimes even at 100°C or isomerization and the polymerization of that resulted from the latter occasionary occur very rapidly and violently, hence there is a case in which the resulted heat of reaction makes $C_2H_4 \cdot O$ break into CO and CH_4 completely via acetaldehyde.

When a small quantity of catalyst is used (below 10% (weight) of $C_2H_4 \cdot O$) polymerization or isomerization and formation of resin are completed at a sufficiently slow pace without producing dangerous high temperature and high pressure. The polymerization will occur at the boundary of gaseous $C_2H_4 \cdot O$ and liquid glycol or commence along with the dissolution of the former into the latter. It is concluded from other polymerization and condensation processes that, according to Burk and Grumitt[27], steps of polymerization reaction are probably little related to the collision factor and activation energy, but these will chiefly depend on the heat conductivity from glycol to $C_2H_4 \cdot O$ at the boundary and the velocity of dissolution into glycol, for the polymerization reaction decreases with increasing of molecular weight though the number of molecules which collide with the boundary is proportional to the root of temperature. By the way the thermal conductivity of $C_2H_4 \cdot O$ increases with temperature (0.00003785 cal.-cm./sec./cm². /°C at 70°C) on the other hand that of ethylene glycol decreases ($x = 7.25 \times 10^{-4} - 1.8T \times 10^{-7}$, where $x =$ thermal conductivity, $T =$ temp.)

According to P. B. report, in Germany $C_2H_4 \cdot O$ is delivered into reaction vessel almost as liquid in the aid of the pressure of Nitrogen, for different from gaseous $C_2H_4 \cdot O$ the liquid has no danger of explosion. The latent heat of vaporization at

760 mm. Hg, 10.5°C is 6082 cal./mole calc.

Effect of Temperature : This is the most important factor. It is held at 120–130°C in I. G. Farben A–G Ludwigshafen am Rhein. In order to retain the temperature at this range, the addition velocity of $C_2H_4 \cdot O$ is largely controled, taking into account of the relation between heat emition and reaction velocity. The delivery of $C_2H_4 \cdot O$ is controled by means of N_2 pressure for safety. Towards the end of the reaction, namely near M.W. 4000, the quantity of liquid becomes 86.5 times of glycol, hence the density of active reacting radicals becomes fewer, and as decreasing the occasion of collision between $C_2H_4 \cdot O$ and the distributed reacting radicals, the absolute quantity of catalyst to promote the reaction will become shorter, decreasing the absorption velocity of $C_2H_4 \cdot O$.

At Hüls chemical faculty in Germany the reaction is performed at 150°C, accordingly the produced oxydwachs cannot bleach and purify by any means, moreover the yield is lower by 5~2%, and m.p. is 45°C or half liquid at room temperature.

The reaction temperature is the lower, the mean degree of polymerization P becomes the larger. In fact at the range 110°~170°C $\triangle P$, the difference between larger and smaller P, is about 20. In the reaction temperature about the range 150~170°C, the relation between polymerization and depolymerization balances at about P=70 as the equilibrium point[2], hence it is impossible to obtain the larger P than this point at this temperature range.

The quantity of catalyst being 0.2~1% (weight) is generally used,[2] anyhow it is conditioned by the standard of ashes in the manufactured goods. Polyethylene-oxide consists of only linear molecules, and as the difference between number mean and weighted mean degrees of polymerization is small, it is considered to be small of its inhomogeneity[2].

It is not right to conjecture the molecular weight from only the range of freezing point. In the fixed values of the absorption quantity of $C_2H_4 \cdot O$ and the quantity used of the same catalyst, how affects the reaction temperature to the degree of polymerization is as follows[2]:

Catalyst	Reaction temp.	m.p.	D.P.
KOH	125~135°C	44–55°C	75.5
KOH	90~100°C	47–59°C	124.7

Those reactions, however, are like the followings ; namely, $C_2H_4 \cdot O$ is passed through the tower filled by catalyst, and in this case $C_2H_4 \cdot O$ is polymerized to polyglycol at the surface of catalyst. Then the polyglycol flows out into a receiver from the bottom of the tower. This reaction type is said to avoid easier the depolymerization than the usual gas–liquid reaction in Batch system, the optimum temperature of the former being 125°~135°C.

Depolymerization is seen to be promoted when the polyethyleneglycol is heated

contacting with air. The degree of polymerization is unchangeable at the heating below 140°C. H_2O is unrelated probably to the depolymerization. Together with the mutual occurance of growth and depolymerization, the polymerization reaction stops at the limited point of fixed mean degree of polymerization determined by the reaction temperature on the whole (this is infered by the curves of integral distribution function and mass distribution function).

Table 2   Changes in degree of polymerization by heating conditions

No.	D. P.	Method of treatment	Heating time (hour)	D. P.
1	125	dissolved into 7 times H_2O, hydrated at 50°−70°C (100mm. Hg) secondary hydrated in oil bath at 170°C−180°C (100−50mm.)	water bath $1\frac{1}{3}$ oil bath $1\frac{1}{2}$	18
2	90	ditto but the temp. of oil bath is 140°−150°C	$1\frac{1}{3}$	1
3	70	ditto but oil bath, 170°−180°C	$1\frac{2}{3}$	18
4	125	leaving open in a flask at 165°−175°C	oil bath 5	38
5	90	ditto	ditto	47
6	125	in flask with no air (50mm.) at 165°−175°C	ditto	7
7	114	in flask with air (50mm.) at 170°−180°C	ditto	93
8	125	after boiling with 7 times H_2O by reflux, the same as No. 1	boiling 5 dehydration $1\frac{1}{2}$	19
9	125	ditto	boiling 10 dehydration $1\frac{1}{2}$	15

The D. P. in the above table is the values from Staudinger's viscosity rule

$$\frac{\eta sp}{C} = Km \, (D.P.)$$

In H_2O solvent $Km = 1.9 \times 10^{-14}$, and this rule is said to be correct in the range of mean D. P. 50∼150. It is experienced that the sample once measured by Saybolt viscosimeter can not measure again. This fact will perhaps follow from the result of depolymerization rather than the change to another substances. The chain of polyethyleneglycol decomposes at over 300°C to a mixture of a very little acetaldehyde, acrolein and besides unsaturated products of high boiling point[5]. The temperature used for addition polymerization of $C_2H_4 \cdot O$ is different with respective alcohol. For instance, in the addition polymerization to nonyl alcohol the temperature range is 160°∼170°C, for oleyl alcohol it is near 170°∼180°C. Of course the temperature used is altered depending on uses. As the critical temperature of $C_2H_4 \cdot O$ is 195.8° C, the reaction is carried out at most below 180°C. It is said that in the case of
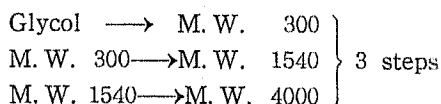
below 140°C the D. P. is almost unchangeable[2]. The reaction temperature for polyethyleneglycol aimed at M. W. below 4000 is optimum in the range 120°~130°C at ordinary pressure not to depolymerize.

Cause of Colouring in the Course of Polymerization

The cause of colouring is perhaps due to the isomerization into acetaldehyde and the formation of aldehyde resin, beside this, according to circumstances, it may be due to the oxydation by $C_2H_4 \cdot O$ and depolymerization with it

Outline in the Polymerization Reaction and Procedure of Polyethyleneglycols.

(1) Steps of Polymerization

$$\left.\begin{array}{l} \text{Glycol} \longrightarrow \text{M. W.} \quad 300 \\ \text{M. W.} \quad 300 \longrightarrow \text{M. W.} \quad 1540 \\ \text{M. W.} \quad 1540 \longrightarrow \text{M. W.} \quad 4000 \end{array}\right\} 3 \text{ steps}$$

(2) Glycol $\longrightarrow$ M. W. 300

Catalyst: NaOH; 0.05% of the product, namely M. W. 300 in this case.

Pressure: 0~5 cm. Hg over 1 atm.

Reaction Temperature: 130°C

End Point of the Reaction: Increase of the Liquid to the fixed Quantity. (4.4~4.9 times of starting glycol.)

(3) M. W. 300 $\longrightarrow$ M. W. 1540

Performed as the same way as in the above case namely Glycol $\longrightarrow$ M. W. 300, the end point of the reaction is the increase of 4.2~4.7 times in volume.

(4) M. W. 1540 $\longrightarrow$ M. W. 4000

Catalyst: NaOCH$_3$; 0.1% of M. W. 4000 produced.

End Point of the Reaction: Increase of 2.5~2.8 times (56.2 times of the first glycol) in volume.

(5) Yield for $C_2H_4 \cdot O$: 90~96%

(6) $C_2H_4 \cdot O$ used contains 0.02% or below acetaldehyde.

(7) Addition Method of Catalyst.

In order to reach the fixed concentration of Alkali in the product, add the computed amount of NaOH dehydrated by fusion at one time at the beginning for every step (for example, NaOH is 0.26% of glycol until M. W. 300).

(8) Addition of Catalyst.

Granular NaOH of first grade dehydrated by fusion is added at 130°C into glycol which is already passing through from the room temperature by $C_2H_4 \cdot O$

An example of using Catalysis: Let the fused NaOH of first grade flow to cool on a plate of iron, and destroy it in comparatively large granular forms for using. Large granular CH$_3$ONa is added in polyethyleneglycol dissolved in a small test tube, then add another polyethyleneglycol to this hot liquid to cover CH$_3$ONa with fusing. This CH$_3$ONa covered with polyethyleneglycol is used as catalyst taking up by pincet and adding into the vessel at 130°C on bubbling with $C_2H_4 \cdot O$.

(9) Reaction Condition

Vessel of porous plate (Fig. 2) is locally of uniform temperature and the reaction probably progresses at both upper and lower part of the vessel on the same velocity.

(10) Excessive Passage of $C_2H_4 \cdot O$

It is desirable for $C_2H_4 \cdot O$ to pass through excessively from the bottom and large quantity of the gas which runs away from the surface is made for glycol to absorb by the pressure of $2 \sim 3$cm. Hg, collecting $5 \sim 20\%$ $C_2H_4 \cdot O$.

(11) Control of Passage

The reaction is controlled by the equation:

$$\triangle H = P - (p + h + R)$$

Fig. 2 Spouting up vessel for polymerization of $C_2H_4 \cdot O$.

(see Fig. 2) by this equation bubbling condition and reaction velocity are determined. $\triangle H$ depends on the viscosity.

Optimum $\triangle H$: glycol $\longrightarrow$ M. W. 300; $1.8 \sim 2.0$cm Hg

M. W. 300 $\longrightarrow$ M. W. 1540; $1.3 \sim 1.6$cm Hg

M. W. 1540 $\longrightarrow$ M. W. 4000; ~ 0.6cm Hg in this case,

$\triangle H$ is almost constant under well controlled state, showing

$\triangle H = 0.62$cm Hg. in the last step.

(12) Reaction Times

Step	Magnification of the Liqued	hours
Glycol $\longrightarrow$ M. W. 300	4.4~4.9	7
M. W. 300 $\longrightarrow$ M. W. 1540	4.2~4.7	8
M. W. 1540 $\longrightarrow$ M. W. 4000	2.5~2.8	8
total	56.2	23

(13) Colouring Situation by the Reaction Temperature and Times.

When the reaction temperature is the higher, the absorption velocity of $C_2H_4 \cdot O$ becomes the larger, and when it is the lower, the reaction is prolonged, in both cases of the above the colouring becomes the stronger.

Consideration: In order to avoid the colouring the followings will be mentioned for the present:

(1) Remove the acetaidehyde in glycol as perfectly as possible.

(2) Refine ethyleneoxide from acetaldehyde.

(3) Make so as not to isomerize $C_2H_4 \cdot O$ to acetaldehyde.

(4) Study how to suppress the reaction velocity of aldehyde resin formation and to promote the polymerization of $C_2H_4 \cdot O$ only.

Preceding to raise till the reaction temperature, 130°C, $C_2H_4 \cdot O$ is passed through glycol, secondary the temperature is raised. By means of this procedure the
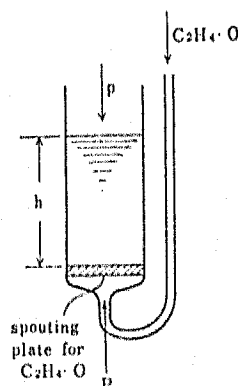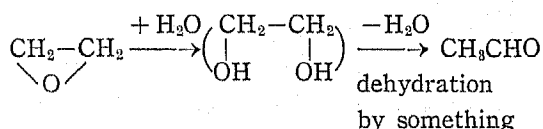
solubility difference between glycol and $C_2H_4 \cdot O$ acts effectively, namely aldehyde in glycol is delivered in $C_2H_4 \cdot O$ and aldehyde is removed together with excessive $C_2H_4 \cdot O$ which runs away from the system, moreover by bubbling out with excessive $C_2H_4 \cdot O$ the aldehyde in glycol tends to get out. This procedure should be performed from the room temperature, for it was done after the temperature raised the aldehyde in the system may happen to polymerize according to circumstances. NaOH is added after this procedure.

About the dehydration from NaOH catalyst is already indicated by I. G. Farbenindustrie. [28,29] Dehydration by fusion of NaOH and KOH, for example, is used for weakening of the colouring to reddish brown on making ethylalcoholate. Colouring is considered from two reasons; the one is the acceleration of isomerization and the other is the promotion of condensation of aldehyde. According to "Petroleum Chemicals" about the isomerization, there are two cases of the isomerization, viz. via vinyl alcohol as an intermediate and by the existence of H_2O. The isomerization of $C_2H_4 \cdot O$ emits heat $(\triangle H = -23.3 \text{ kcal.})$ and it is capable under any real condition. Generally it goes on with evolving heat at $300° \sim 400°C$, and at $150° \sim 300°C$ isomerization is performed by dehydrating catalysts such as Almina, phosporic acid and metal phosphate, [30] in the latter case ethyleneglycol and other hydrated compounds are produced as byproducts.

$$CH_2-CH_2 \xrightarrow{+ H_2O} \left(\begin{array}{cc} CH_2-CH_2 \\ | \quad\quad | \\ OH \quad OH \end{array} \right) \xrightarrow[\text{dehydration}]{- H_2O} CH_3CHO$$
by something

NaOH of first grade usually contains 10% H_2O. By the study of two molecular condensation of aldehydes, it is clear that the condensation of acetaldehyde is promoted by Alkali along with coexistence of H_2O. In the existence of H_2O NaOH gives $-OH^-$ion, and the condensation velocity depends proportionally on the linear power of $[-OH^-]$. This condensation is second order at the beginning. Heat of this reaction calculated is given as 4.81 kcal., but it is said that the experiment gives larger value.

It is very effective to use NaOH immediately after the preparation by fusion. The activity of NaOH becomes weak, if it is used after a long time elapsed, namely by absorbing H_2O, it causes colouring and the extra process: $H_2O \rightarrow$ glycol $\rightarrow$ polyethyleneglycol is participated.

According to experiment, the colouring is the less, if NaOH is the more strongly dehydrated by fusion, on the contrary if H_2O is added with equal amount of NaOH, the colouring decreases. From this fact the author considers as follows, namely, the trace of H_2O will probably influence on the dehydration faculty of NaOH in the

same way as the case of $CaCl_2$ in which its hygroscopicity becomes maximum with some water of crystalization. By the way NaOH has deliquescence property and is easily soluble in H_2O evolving plenty of heat. Its solubility is 109g/100gH_2O and it is soluble in alcohol and glycerine. The melting point of monohydrated NaOH is 64.3°C. NaOH is not decomposed into H_2O and oxides by heating. According to the above equation aldehyde will appear by dehydration with the aid of NaOH and polymerized to coloured resin by the same NaOH as catalyst, hence polyethylene-glycol produced is coloured. It is observed that after adding NaOH the surface of NaOH is covered with brown layer on getting 70~80°C. As already mentioned the melting point of monohydrate is 64.3°C, and so NaOH gained sufficient H_2O is fused with the resulting in the dehydration of glycol to acetaldehyde, making the coloured resin.

It is seen that glycolate produces successfully at 130°C or near. If glycolate is needed for the polymerization process as an intermediate, it is desirable to add NaOH catalyst at the temperature suitable to make glycolate, namely NaOH dehydrated by fusion previously and glycol both heat to 130°C and then the former is added into the latter. It is understood from the above reason why the all references state to use dehydrated NaOH.

If there is almost no water along with NaOH, glycol is more possible to become glycolate rather than acetaldehyde. When there is great quantity of NaOH, the water produced by formation of glycolate strengthens still more the power of dehydration of NaOH, therefore a great quantity of dehydrated NaOH also can give coloured polyethyleneglycol. Even stored in P_2O_5 desiccator the effect of dehydrated NaOH becomes weaker.
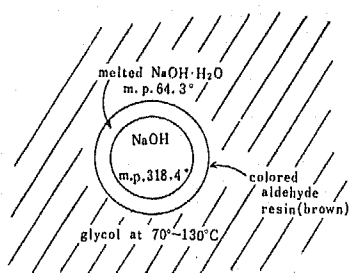

Fig. 3   Granular NaOH in hot ghycol.
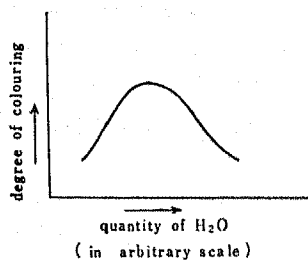
Fig. 4   An illustration about appearance of opposite results in the both sides of the maximum

When there is a little larger quantity of H_2O, NaOH loses its dehydration power, hence colouring diminishes with increasing H_2O. Therefore there will be a maximum about the colouring strength vs. quantity of H_2O as illustrated in Fig. 4.

However, from the view-point of the efficiency of manufacturing polyethyleneglycol, it can not adopt to avoid the colouring by using larger quantity of H_2O, for the production of glycol from H_2O is especially slower in the case of alkali catalyst, moreover H_2O bound to glycol by hydrogen-bonding is not easily driven out the system, hence the reaction velocity decreases.

From the above consideration NaOH should be used after dehydration. Glycol reacts with nearly a half of the NaOH forming glycolate at 130°C. Glycolate is also produced by the following equation,

$$CH_2 - CH_2 + NaOH \longrightarrow CH_2ONa.$$
$$\diagdown O \diagup \qquad\qquad CH_2OH$$
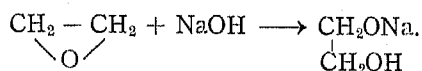
But this reaction perhaps carried out in a field of dissociating agents such as H_2O or glycol etc.

It is found that $C_2H_4 \cdot O$ is a little isomorized to acetaldehyde on passing through glycol at 130°C. Therefore if $C_2H_4 \cdot O$ is passed through in the extent that there is no running away of excessive $C_2H_4 \cdot O$, the produced acetaldehyde is accumulated as time goes on and consequently the product is coloured. Hence in order to avoid the colouring the excessive $C_2H_4 \cdot O$ should be run away from the system and the latter quantity of excess is sufficient below 5% of used $C_2H_4 \cdot O$. Even regarded as this excessive part is all lost, the yield of polyethyleneglycol attains to 90~96% with white product.

By this extent of excessive $C_2H_4 \cdot O$, after one hour from the beginning of every step, a faint colour produced is gradually lost and finally almost missing. The larger the molecular weight becomes, the faster the coloured matter which is produced by the catalyst added is lost. It is not economical that the matter lost by excessive passing of $C_2H_4 \cdot O$ is not only the colouring cause but also glycol itself, moreover $C_2H_4 \cdot O$ once passed through and partly missed by the isomerization is collected in a large quantity to purify accompanying the loss of washing by calcium carbonate and of drying by a desiccative.
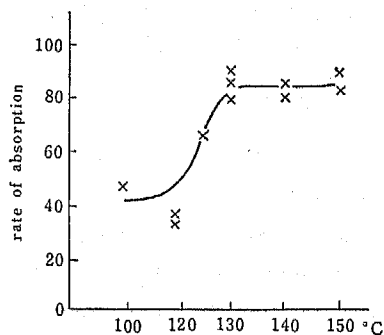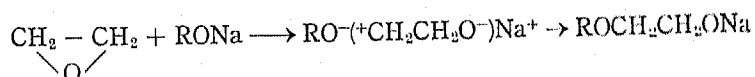
The temperature of 130°C in the above reaction (3) gives the maximum yield of glycolate, furthermore on the manufactuing of polyoxyethylenealkylether which is synthetically polymerized with $C_2H_4 \cdot O$ from lauryl alcohol, the temperature of 130°C or near so is the optimum temperature extremely effective for the reaction (Fig. 5). It is generally accepted that Na atom adds to free radical, hence it is perhaps said that the position to which Na tends to add has a property of free

Fig. 5   Absorption of $C_2H_4 \cdot O$ by lauryl alcohol (1% wt. KOH catelyst)

radical. From this view-point it is better to consider that the polymerization by Alkali metal is an addition reaction rather than catalytic reaction.
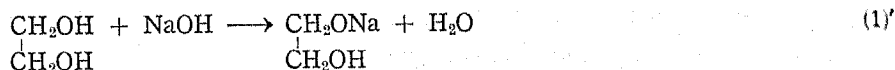
$$CH_2 - CH_2 + RONa \longrightarrow RO^-(^+CH_2CH_2O^-)Na^+ \rightarrow ROCH_2CH_2ONa$$
$$\diagdown O \diagup$$

If it is so, as regards to the addition reaction of $(C_2H_4) \cdot O$, this is what makes the stem to which $C_2H_4 \cdot O$ may be added, it is natural that the reaction requires the temperature of 130°C with Alkali catalyst. At all events in the polymerization of $C_2H_4 \cdot O$ at the range, 125~130°C, the absorption velocity of $C_2H_4 \cdot O$ and the yield of polyethyleneglycol are found to be the maximum.

Experiments of Isomerization at 130°C with regard to $C_2H_4 \cdot O$: Add $C_{10} \sim C_{12}$ paraffin hydrocarbon in a flask, suspend fine powdered (dehydrated) KOH (1% weight) in it, then at 130°C pass $C_2H_4 \cdot O$ which was refined by soda lime (acetaldehyde content is 0.001%) through the flask. In this case at the first place the surface of KOH is coloured to brown and after 8 hours the liquid part is coloured too. And the surface of KOH becomes reddish brown. As the weight of the content in the flask does not increase, it is seen that the polymerization of $C_2H_4 \cdot O$ does not occur. Even when $C_2H_4 \cdot O$ used in this experiment is again condensed, no aldehyde being analyzed in it, From this experiment it is shown that, as aldehyde is catched by KOH, it is possible to remove aldehyde from the medium.

Further, after heating paraffin only at 130°C, and then pass $C_2H_4 \cdot O$ through the former, the liquid is coloured in a faint yellow and aldehyde increases to 0.01% in the collected $C_2H_4 \cdot O$.

Experiments on the Formation of Glycolate: The reaction;

$$\begin{array}{l} CH_2OH + NaOH \longrightarrow CH_2ONa + H_2O \\ | \hspace{8em} | \\ CH_2OH \hspace{5.5em} CH_2OH \end{array} \hspace{4em} (1)'$$

is performed at the ratio (glycol:NaOH = 5mole:1 mole) in order to remove H_2O in the right hand side by the hygroscopicity of glycol. If in this system $ClCH_2 \cdot CH_2OH$ is added, the reaction

$$\begin{array}{l} \hspace{10em} CH_2OH \\ \hspace{10em} | \\ CH_2OH + CH_2OH \longrightarrow CH_2O \diagdown \hspace{2em} + NaCl \\ | \hspace{4em} | \hspace{11em} \diagup O \\ CH_2ONa \hspace{2em} CH_2Cl \hspace{2.5em} CH_2 \\ \hspace{14em} | \\ \hspace{14em} CH_2OH \end{array}$$
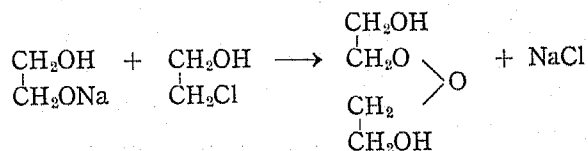
will occur. In the reaction at a range 80°~150°C, the maximun yield(55%) was obtained at 130°C. From this point of view, the yield of the reaction (1)' willbe max imum at 130°C and its value may perhaps fall in a range 50~60%. Therefore, the optimum temperature about the polymerization of $C_2H_4 \cdot O$, namely 130°C, is the temperature of the maximum formation about glycolate too, and in both reactio ns Na is in common.

Experiment on Colouring of Lauryl-alcohol by Caustic Alkali : Lauryl alcohol in the market contains as impurities higher aldehydes besides alcohols of homologous series and it shows remarkably the qualitative reaction of aldehyde such as Tollen's reaction. Lauryl alcohol which was shaked sufficiently with concentrated $NaHSO_3$ solution below at room temperature and then distilled in vacuum was used. Lauryl alcohol from the market and the refined lauryl alcohol were added by 1% weight KOH respectively and held for 8 hours at 130°C, than the former growed yellowish as time went, after 8 hours it showed yellowish brown, but the latter was not coloured at all.

The Extent of Colouring by Aldehyde when $C_2H_4 \cdot O$ is polymerized with Lauryl-alcohol by 1% KOH Catalyst: Reaction temperature, 130°C; reaction time, 8 hours; absorbed $C_2H_4 \cdot O$, about 10 moles.

No.	lauryl alcohol	acetaldehyde % contained in $C_2H_4 \cdot O$	colouring
1.	lauryl alcohol from the market	0. 92	strong reddish brown
2.	〃	0. 40~0. 45	reddish orange
3.	refined alcohol by $NaHSO_3$	〃	〃
4.	〃	0. 1	orange
5.	〃	0. 01	yellowish brown
6.	〃	0. 001	yellow

From the above data colouring cause by acetaldehyde, its situation, and tendency are understood. If operated skillfully No. 6 as a matter of course should has no colour. When KOH dehydrated by fusion was used, colouring was weaker than other cases.

Yellow resin: By heating alcoholic potash with aldehyde, a yellowish brown resin is isolated. [32]

Red resin: When aldehyde is heated in aqueous solution with KOH, the solution at once shows yellow along with becoming muddy, then rapidly produces reddish brown matter (which is able to prolong in a long fiber[33]). This becomes dark with increasing of the quantity.

In acetaldehyde solution the formation of aldehyde resin only is not the final product but there are acetate, ethylalcohol, higher aldol and yellow and red resins etc.

Formation of Acetaldehyde by Decomposition of Ethyleneoxide: This is confirmed by the determination of acetaldehyde by means of precipitation of mercury from the product of decomposition by heat of ethyleneoxide[34] at 400°C (initial $C_2H_4 \cdot O$ concentration is 0. 04220g. mole/l.), (by mercuryoxide method).

time, (minutes),	30,	40. 5,	57,	65,
aldehyde, %,	0. 00090,	0. 00095,	0. 00028,	0. 00062,

The maximum quantity of acetaldehyde was only 2% of $C_2H_4 \cdot O$ at most, recognized by means of Schiff's method. From these results Seddon et al. regarded that acetaldehyde is perhaps not the product from the decomposition of $C_2H_4 \cdot O$. They say that the decomposition coefficient by heat (temperature coefficient) of $C_2H_4 \cdot O$ is much larger than that of acetaldehyde.

Besides, Winfield et al.,[35] Kraussky[36], Jpatiew and Leontowitsch[37], Nef[38], and Peytral[12] carried out the study of decomposition by heat. In some cases the decomposition seemed to be heterogeneous and in other case (Winfield et al.) it was strictly homogeneous.

Melle Peytral[12] studied the mean temperature of decomposition to occur by means of a platin tube making $C_2H_4 \cdot O$ gas pass through the latter within 60 seconds. The produced gases were besides H_2O and CH_3CHO,

$$CO \cdots 44.7\%, \qquad H_2 \cdots 28.3\%, \qquad CH_4 \cdots 15.0\%$$
$$C_2H_2 \cdots 5.0\%, \cdots C_4H_8 \cdots 7.0\% \qquad (total\ 100\%)$$

The reaction reasonably conjectured were as follows:

       first order reaction   mean propotion of decomposition

(1) $4\ C_2H_4 \cdot O \longrightarrow 4HCHO + C_4H_8 \cdots 0.54$

(2) $C_2H_4 \cdot O \longrightarrow H_2O + C_2H_2 \cdots 0.09$

(3) $C_2H_4 \cdot O \longrightarrow CH_3CHO \cdots 0.37$
     second order reaction

(4) $CH_3CHO \longrightarrow CO + CH_4$

(5) $HCHO \longrightarrow CO + H_2$ (completely)
     third order reaction

(6) $CH \equiv CH + H_2 \longrightarrow CH_2 = CH_2$ (trace)

Decomposition coefficient from (3) to (4) was calculated as 0.926, and so one $C_2H_4 \cdot O$ molecule was isomerized to 0.03 molecules af CH_3CHO. She calculated from the heat of formation that the combustion of 1g. mole $C_2H_4 \cdot O$ releases a heat of 13.21 (kcal. /mole) at constant pressure. The mean rising of the gas temperature due to combustion was calculated as 629°C and one volume of $C_2H_4 \cdot O$ changed to 2.05 volume of other molecules. From the number of particles which passed through the platin tube and its velocity, the temperature of the gas was calculated to rise from 571° to 1200°C within 0.002 second.

In the homogeneous decomposition carried out by Winfield in a pyrex tube, the velocity of decomposition depended on the equation of Arrhenius and on the activation energy of this decomposition was obtained as 52 kcal.

The heat of isomerization Q, which is a little different with respective author, is calculated from the heat of combustion given by Berthelot:

ethyleneoxide : 6870 cal. /g (Ann. chim. phys. [5] 27, 374 (1882))

acetaldehyde : 6338 cal./g (Compt. rend. *129*, 920 (1899))
as Q=23.3 kcal.

It is said that ethyleneoxide in a tank of iron decomposes slowly at room temperature, and 18% of $C_2H_4 \cdot O$ from that tank of iron can not be absorbed by H_2SO_4, the latter part being analyzed to be consisted from 50% of CO.

According to WINFIELD et al.[35] there is an induction period at the beginning of decomposition about C_2H_4O, this period is 1.5 minute at 444°C, 5 minutes at 400°C and much prolonged at lower temperature. The final products and pressure change about the decomposition in a pyrex tube at ca. 400°C were as follows[35];

	expt.	expt.	expt.		expt.	expt.
H_2%	6.2	7.8	7.9	initial pressure mmHg	30.92	23.21
C_2H_6%	6.6	7.7	7.0	final pressure //	61.86	46.42
CH_4%	37.5	35.1	35.3			
CO%	49.6	49.0	49.9			

Depending on stirring condition in the reaction system, some local superheating can occur, when the above decomposition and continued isomerization will take place and the product is coloured in the polymerization reaction to polyethylene-glycol.

WINFIELD concluded that in spite of a strong odor of acetaldehyde in the decomposition products from $C_2H_4 \cdot O$, acetaldehyde was not found at least by his analysis, almost all the acetaldehyde which as long as formed by decomposition of $C_2H_4 \cdot O$ got through to decompose. It seems that it will grow to high polymer and to coloured matters, if acetaldehyde should be in the condition of polymerization.

Decolouring of Aldehyde Resin

EKEKRANTZ[39] divided yellow resin (already mentioned) into two kinds, namely α-resin which is soluble in benzene and β-resin which is hardly soluble in it. These were considered to be isomer. Its molecular formula was given as below:

$$(12CH_3CHO - 6H_2O =) \ C_{24}H_{36}O_6$$
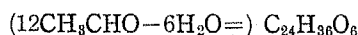
These have two ethylene bonds in a molecule, being oxidized by H_2O_2 in glacial acetic acid, a white acid $C_{18}H_{24}O_6$ was obtained, and he could not make any derivative distinctly defined by sulfonating, acetylating or hydrolysis from these. By synthetic consideration from various results the following formula was conjectured after all.

$$CH\ CH\ -\ \overset{\shortmid}{CH}\ -\ CH$$
$$\overset{O\ \diagdown\diagup\ O}{\underset{CH\ CH\ =\ CH\ -\ CH}{}}$$
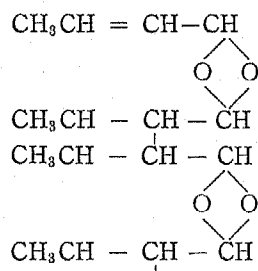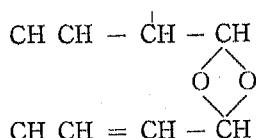
From this view–point the author considers that decolouring of polyethyleneglycol by means of H_2O_2 produces $C_{18}H_{24}O_6$ as one of the oxidation products, as H_2O_2 itself does not affect polyethyleneglycol according to P. B. report.

Influence on the Decomposition of $C_2H_4\cdot O$ by foreign Gases. [35]

It is said that the velocity of decomposition "k" of $C_2H_4\cdot O$ decreases depending on the complexity of hydrocarbon added as inert gas. N_2 and CO decrease k in the same way, and CO_2 which has somewhat larger degree of freedom and larger cross section of collision decreases k somewhat largely, even if the travelling velocity of the latter is small. Argon and Neon less decreases k than any other gases, for their collision is the most elastic and they have only three degrees of freedom. Helium decreases k remarkably.

From the experience that if the glycol which is blowed by N_2 somewhat for a long time before the beginning of polymerization is used the polyethyleneglycol is less coloured than otherwise, it will be useful to blow the matter, which likes to CH_3CHO in structure and mutually soluble easily with acetaldehyde, into glycol with $C_2H_4\cdot O$ in order that acetaldehyde runs away from glycol and not to colour the polyethyleneglycol. In fact it was already mentioned that the method in which some excessive $C_2H_4\cdot O$ of 2~5% is made to run away from the system is necessary not to colour the polyethyleneglycol. In this case "the matter" mentioned above is $C_2H_4\cdot O$ itself.

$$CH_2\!\!-\!\!-\!\!-\!\!CH_2 \overset{k}{-\!\!\!\longrightarrow} CH_3CHO\ (active)\ +23.3\ kcal.$$
$$\diagdown O \diagup$$
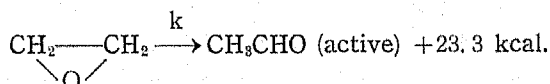
The graph, $-\log k$ versus $\dfrac{1}{T}$ (T=the absolute temp.), forms straight line completely, and from the slope the activated energy was obtained as 52 kcal.

Influence of Hydrogen: When HINSHELWOOD[36] studied the decomposition of diethylether at low temperature, he found that with sufficient coexistence of H_2 it revived a velocity of higher coercive decomposition. He explained this as follows; namely by flying lightly with high velocity and performing many collisions the H_2 gas which exists among the colliding molecules might be particularly so adequate in order that diethylether holds the energy near its own MAXWELL distribution. It seems that other gases than H_2 have no such property.

According to the decomposition experiment of $C_2H_4\cdot O$ in H_2 gas of one atom·osphere pressure, the velocity of decomposition increased by about 40% per every degree of the temperature. Activated energy obtained from this experiment was

51.5 kcal. agreed with above value 52 kcal. within the error of experiment. In fact there is a report in which on decomposing of $C_2H_4 \cdot O$ at 125~150°C with Nickel catalyst in H_2 gas acetaldehyde, crotonaldehyde, and other products were obtained. [37] When Na is used as catalyst H_2 will be produced, and the isomerization of $C_2H_4 \cdot O$ is perhaps promoted by H_2 as well as by Alkali and the heat, hence after making glycolate sufficiently it is necessary to remove the staying H_2 from the system thoroughly before the beginning of the polymerization.

Measurement of the Molecular Weight of Polyethyleneglycol.

The measurement of molecular weight is the first prescription of polyethyleneglycol. The ascent of boiling point method can not be used in this case. The descent of freezing point method is used for a measurement of the molecular weight below 10,000 and hence can be adopted for polyethyleneycol of this case, besides viscosity method, osmotic pressure method and supercentrifugal method can be used. The values obtained by such methodes are the plysical molecular weight and give the quantity of particles in a liquid. It was verified by the school of STAUDINGER that the above physical molecular weight agrees with chemical one. Whether a molecule is a giant molecule is established by the agreement between the physical molecular weights and that of its chemical derivatives. The reaction used in this case is called the conversion of polymer analogues.

According to KRARMER and LANSING, [40] the mean value of molecular weight is divided into three kinds depending on methods of measurement:

$$\text{number mean} \quad M_n = \frac{\sum M_i \, N_i}{\sum N_i}$$

$$\text{weighted mean} \quad M_w = \frac{\sum M_i^2 \, N_i}{\sum M_i \, N_i}$$

$$Mz \quad \text{mean} \quad M_z = \frac{\sum M_i^3 \, N_i}{\sum M_i^2 \, N_i} ,$$

where Mi is the i-th molecular weight in unit volume, and Ni is the number of molecules having the i-the molecular weight in unit volume.

(1) **Terminal group method**: Polyethyleneglycol has one and one $-OH$ group at the both ends, therefore, they are refered by P. B. report as hydroxyl number of polyethyleneglycol for a factor which prescribes the property of polyethyleneglycol. $-OH$ group at the end is quantitatively acetylaled or methylated easily, and there is agreement between the descent of freezing point method concerning the original dihydroxyl compound and the measurement of the newly included acetyl group.

(2) **Viscosity method**: This method originates in Stauinger. [41]

$$\lim_{C \to 0} \eta_{sp}/C = K_m. \, P$$

$$\lim_{C \to 0} \eta_{sp}/C_{gm} = K_m. \, M.$$

where P = degree of polymerization, C = concentration g. /l. , C_{gm} = concentration (monomer mole/l.), K_m = Staudinger constant, and η_{sp} = specific viscosity. Since polyethyleneglycol fortunately has a fixed structure, K_m is definite constant and these equation can be used for determination of molecular weight. If a molecule has side chains and it is formed of various shapes, K_m might not be fixed and depend on its synthetic methods, therefore, in the latter case these equations can not be used. These equations can not be also applied in the case of heteropolar linear molecules or remarkably bending molecular forms.

It is experimentally known that there is a linear relation between η_{sp}/C and η_{sp}, hence utilizing this relation there is a handy SCHULZ and BLASCHKE's method of calculation. Since η_{sp}/C in the STAUDINGER's rule is proportional to the length of molecular chain, STAUDIGER gave a formula

$$\lim_{c \to 0} (\eta_{sp}/C) = K_{eq} \cdot N$$

where K_{eq}. is designated as "molecular chain equivalent constant" and N is number of chain members. In the above formula the value of η_{sp}/C shows that for the increment of one more atomic group there is a fixed increase, where for the value of η_{sp}/C the case of lim. $C \to O$ should be taken. In the case of polyethyleneglycol $N = 3P + 1$, for n is the number of atomic group forming linear main chain but not side chain.

The molecular chain equivalent is obtained as monomer weight divided by n of monomer molecule, namely in the case of ethyleneoxide it is 44/3. n is obtained on dividing molecular weight by molecular chain equivalent and plus 1 to its result.

FORDYCE and HIBBERT[43] studied about the polyethyleneglycol, and the characteristic feature of their experiment consists in the study of Staudinger's rule of viscosity about the polyethyleneglycol having specific and simple molecular weight.

General viscosity formula for molecules of various froms is

$$\eta_{sp}/C = K \cdot P^n ,$$

where n is conjectured as it is in the range $0 \sim 2$, namely n = 1 holds for a fairly bending linear molecule, $n = \dfrac{1}{2}$ holds for freely bending linear molecule and n = 2 holds for straight molecule like rod. [44] From this view–point it may safely be said that polyetyleneglycol is a fairly bending linear molecule.

(3) **Osmotic presure method**: Molecular weight is obtained from the following Van't Hoff's equation

$$M = RT. C/p,$$

where M = molecular weight, p = osmotic pressure, C = concentration, T = absolute temperature, and R = gas constant. According to SCHULZ[45]

$$p = \frac{RTC}{M(1-CS)},$$

where S=specific volume. Linear relation between logp and logS gives a garantee of the possibility about its application.

(4) **Supercentrifugal method**: This is one of the most reliable method and at the same time the distribution of molecular weight is found.

(5) **Distillation at constant temperature method** : Since this method is said to be adequate to a range of molecular weight 5000~20000, but for polyethyleneglycol which is generally below 4000 it can not be used.

(6) **Diffusion method**: Diffusion phenomenon is a slow one, hence it is not good from the view-point of taking much time.

(7) **Dialysis coefficient method** : This method is not good for a molecule which consists of linear large molecule. About the molecular weight of polyethyleneglycol, STAUDINGER et al. [46] studied the comparison between this method and the end group method, but the results were almost not agreed.

From the above consideration it is capable of practical use to measure the molecular weight of polyethyleneglycol by means of the following equation adopting the STAUDINGER's viscosity rule and asking for the constant in the above simplyfied method by SCHULZ and BLASCHKE.

$$\lim_{C \to 0} (\eta_{sp}/C) = \frac{SP/C}{1+k\eta \cdot \eta_{sp}} = K_m \cdot P,$$

where C=concentration (g./l.), $K\eta$ = specific constant for polyethyleneglycol, P = degree of polimerization, K_m=Staudinger constant, and η_{sp}=specific viscosity=$\eta_{rel.}$ −1, and $\eta_{rel.}$ =relative viscosity:

$$\eta_{rel.} = \frac{t_1 \cdot d_1}{t_0 \cdot d_0},$$

where t_1=time of the outflowing of solution, d_1=specific gravity of solution, $t_0=$ time of the outflowing of solvent, and d_0=specific gravity of solvent. (in the case of H_2O, t_0=28.6 sec. (25°C) and d_0=0.99707 by Saybolt viscosimeter). The value of K_m has been given by SCHULZ and STAUDINGER, and when P=50~150 it is said that K_m= 1.9×10⁻⁴ is appropriate.

In the case of polyethyleneglycol M. W. 400~1540, the above viscosity rule hardly holds, moreover the density measurement at the measurement of η_{sp} takes considerable time and much labour. Therefore, it seems adequate usually to use the descent of freezing point method for M. W. below 1540. The comparison about the experimental values between the descent of freezing point method and the viscosity rule is:

| | viscosity rule | | descent of freezing point method (benzene) | | |
Sample NO.	η_{sp}	M.W.	P	M.W.	P
1	0.7532	3964	90.1	4075	92.6
2	0.8634	4400	100.0	3990	90.7
3	0.5994	3159	71.8	3090	70.2

From this data they agrees at about P=90, but there is a considerable difference at about p=100; in view of these facts it is perhaps handy to use the descent of freezing point method which take shorter time for dealing with many samples. It is important to select solvents in the case of the descent of freezing point method, for if H_2O is used it differs considerably from the theoretical value even at M.W. about 1540.

It seems that when measuring the viscosity of high polymer of wide distribution the influence of large molecules is particularly stronger. In view of this fact it perhaps dangerous to determine unknown molecular weight by the curve of known molecular weight versus Saybolt viscosity.

However the standards of polyethyleneglycol of U.C.C.C. in U.S.A. is prescribed to name the goods of polyethyleneglycol by the molecular weight corresponding directly to the Saybolt universal viscosity or Centistokes at 210°F (=98.8°C), for instance:

Mean M.W.	190~210,	285~315,	380~420,	570~630,	950~1050,	1300~1600,	3000~3700
Saybolt viscosity, sec. (210°F)	38~ 41,	42~ 46,	45~ 55,	60~ 70,	70~ 100,		
Centistokes	4.3,	5.8,	7.3,	10.5,	17.4,	25 to 32,	75 to 78
freezing point, °C	−15>,	−15 to −8,	4 to 8,	2 to 25,	37 to 40,	43 to 46,	53 to 56
description	200,	300,	400,	600,	1000,	1540,	4000

From the view of this table, it has been given up to use the strict molecular weight for industrial goods to deal with in U.S.A.

According to Flory, he obtained from the distribution of molecular weight concerning polyethyleneglycol the following relation;

$$\frac{M_w}{M_n} = 1 + \frac{\nu}{(1+\nu)^2}$$

where ν=ratio between ethyleneoxide consumed within a certain time and that at the beginning. From this relation, in proportion to the time elapsed, namely as the polymerization progresses, M_w tends to M_n.

ANALYSIS OF ACETALDEHYDE IN ETHYLENEOXIDE

Method by means of Schiff's Reagent

By this method acetaldehyde in ethyleneoxide is analyzed up to 0.002~0.005%. The mechanism of the reaction is said to be as follows.[49];
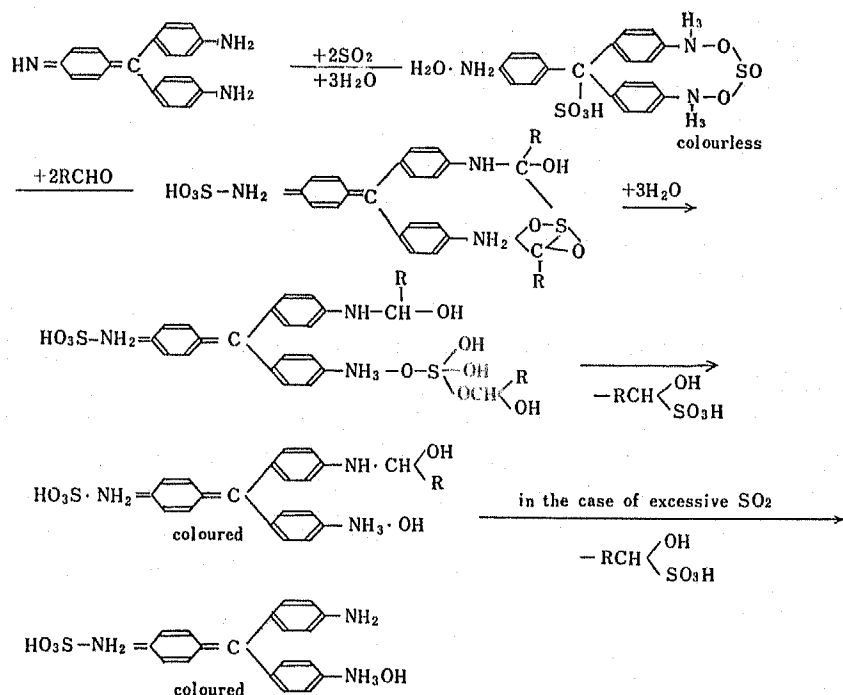
This reaction is hindered by excessive $NaHSO_3$. When performed with unknown sample it is said that pH below 2.6 is suitable. The adjustment of pH is performed by adding an acid or buffer solution to a sample.

Kinds of Preparation of Reagents: There are preparation method of Guyon[50], Crocker and Schimmel[51], Blaser, Schiff and Caro, Gross and Bohle, and Deniges.

It is said that the pure acetone gives this reaction[52] and the latter is also given by unsaturated aldehydes[53].

Example of a Preparation Method used.

Basic Fuchsine : Disslve 0.5g. (0.0015 mole) powdered in warm water of 200 ml. and cool (ceimson).

$NaHSO_3$: Dissolve 6g. (0.06 mole) into water of 100 ml. The mixture of both the above is added by concentrated HCl of 5ml. (0.06 mole) and diluted to 500 ml. This is 0.1% Schiff's reagent. Fuchsine of 1 mole (338g.) is equivalent to acetalde-hyde of 2 mole (88 g.). After letting alone the prepared solution untill discoloured to a faint yellow like straw, it is preserved in a coloured bottle in a dark and cold room. This is fit for preservation for fifty days (at room temperature).

If $NaHSO_3$ is not pure and substantially insufficuent, as the colour of fuchsine appears, the analysis becomes nothing but the comparison of colours between crimson and red violet, and it cannot be carried on. Therefore, it is necessary to hold sufficient quantity of $NaHSO_3$, thus it is appropriate to make the above solution

on determining the 4% of NaHSO$_3$ with the volumetric analysis of the latter. If the substantial quantity is held, whenever the reagent is prepared the situation of the colouring is seen to be the same.

According to the experiment, colouring of 0. 001 % acetaldehyde becomes the maximum. at 25°C after 30 minutes, when 5 ml. HCl in the above preparation is used with 25 ml. acetaldehyde (0. 0000058 mole) and 1ml. Schiff's reagent (fuchsine 0. 000003 mole). Therefore, the colouring is the maximum at the case;

$$HCl \text{ (mole)} = NaHSO_3 \text{ (mole)},$$
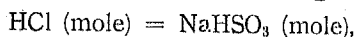
hence the following ratio;

$$\text{fuchsine: } NaHSO_3 : HCl = 1 : 40 : 40 \text{ (mole ratio)}$$

can be adopted.

2ml. of Schiff's reagent is to be used for the concentration of 0. 01 % acetald-ehyde, for in this case the clouring is the maximum. If, however, 0. 001% acetal-dehyde is analyzed, 2 ml. of Schiff's reagent is not adequate. The ml. number of Schiff's reagent depends on acetaldehyde content for its maximum coloring. The optimum quantity of Schiff's reagent corresponding to 0. 01 % acetaldehyde is one fifth of its equivalent.

Influence of Temperature: For 0. 001% acetaldehyde, for instance, the coloring at 25°C is six times stronger than that at 8°C of the solution temperature, hence 25°C is fixed for the comparison of the colour.

Dilution of Ethyleneoxide Sample: Ethyleneoxide is used with dilution of 30 times by H$_2$O, for if the dilution is below 30 times the ethyleneoxide only, even though acetaldehyde is not present, colours by 2 ml. of the Schiff's reagent. When diluted to 30 times there is no influence of ethyleneoxide on measuring in 20 minutes after the preparation and it can be analyzed until 0. 002% concentration of acetaldehyde.

To determine the Concentration of Acetaldehyde in Ethyleneoxide in 20 Minutes after the preparation for analysis: To 25 ml. of ethyleneoxide sample (already diluted to 30 times by volume) add the 2 ml. of Schiff's reagent, then in 20 minutes after the preparation the maximum colouring can be obtained for several kinds of con-centrations of acetaldehyde. The mean time for measurement requires for 5 minutes and within this time many readings can be gained with the minimum error. In the case of 0. 001% concentration of acetaldehyde, on using 0. 2 ml. Sciff's reagent the maximum colouring appears about in 30 minutes after adding.

Colouring by the Distilled Water only: This is seen to be due to the effect of pH. of the solution. On utilizing this phenomenon, even when very low acetaldehyde concentration is included, the % of acetaldehyde content is determined. When 2 ml. of the Schiff's reagent is used, 0. 0001% concentration of aldehyde in the 25 ml. of the prepared solution can be analyzed. As, however, aldehyde is 30 times diluted by volume of ethyleneoxide in order to avoid the intefrerence of the latter, the limit of analysis with respect to the aldehyde in ethyleneoxide sample is 0. 003% at

most. When 0.2 ml. of the Schiff's reagent is used instead of 2 ml., the degree of colouring becomes higher than the latter case in the lower concentration of aldehyde. In the case of higher concentration the situation is reversed, namely the colouring becomes the lower when the reagent used is the less. In the case of using the 0.2 ml., it is also coloured by the distilled water itself (Fig. 6). As seen in Fig. 7 the difference "a" of the colouring strength at the case of using the 2 ml. reagent becomes the larger difference "b" at the using of the 0.2 ml. reagent.
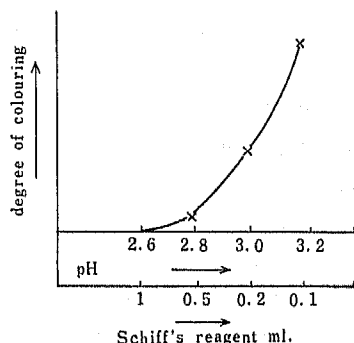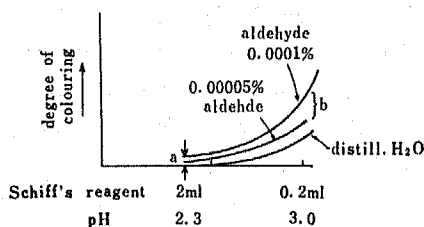

Fig. 6 Colouring of distilled water by Schiffs reagent.

Fig. 7 Colouring of extremely diluted acetaldehyde by Schiff's reagent.

Example of Expriment: Dissolve purified ethyleneoxide which seems not to contain acetaldehyde 4.9995 g. into 50 ml. of 0.001% acetaldehyde solution and dilut to 250 ml. with distilled water, using this as a test solution. This is the aqueous soltion of 1/50 (g./ml.) ethyleneoxide containing 1/500000 (g./ml.) acetaldehyde, namely this solution should contain 0.0002% aldehyde. Add 0.2 ml. of the Schiff's reagent to both 25 ml. of this test solution and of the 0.001% standard solution of aldehyde in water bath both at 25° and after letting alone for 30 minutes, compare the colourings between them:

	After letting alone for 10 min.	
	height of liquid layer	cclouing ratio
standard soln.	15.2mm	1
test soln.	7.6	5.23
	After letting alone for 30 minutes	
standard soln.	15mm.	1
test soln.	80	5.3

From the above values aldehyde content results in 0.0002 %, which is the value estimated beforehand from the test solution.

  Tomoda's Method[54] (Ripper's Method[55])

    The limit of this method with respect to acetaldehyde content in ethyleneoxide is below 0.002% of aldehyde content at the case in which 20 g. of ethyleneoxide is

taken. 0.4 mg. of acetaldehyde in 100 ml., namely the 5 times solution of $C_2H_4 \cdot O$, can be quantitatively analyzed.

Measurement:

(1) Cool a duplicated wlole pipet below 10°C and pipet the 5 times diluted $C_2H_4 \cdot O$ sample of 20 ml. cooled by ice into a Erlenmeyer flask (having its own stopper) of 250 ml.

(2) Add about 1 % $NaHSO_3$ solution by a 10 ml. whole pipet.

(3) After tightly plugging the flask, let it alone in a ice water bath.

(4) On adding 1 % starch solution (0.5 1ml.), titrate this solution with a N/10~ N/100 iodine normal solution, and designate the required volume as A ml.

(5) Add powdered $NaHCO_3$ excessively to that solution so much as undissolved $NaHCO_3$ is always present on the bottom, titrate with the above normal iodine solution and designate the required volume as C ml.

(6) As a blank test, perform the above (2)~(4) at every analysis and designate the required normal solution as B ml.
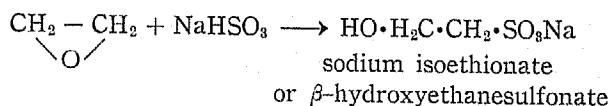
Calculation of acetaldehyde % (in the case of N/10 iodine solution)

$$\text{acetaldehyde \% in a sample} = \frac{0.0022015 \times \left\{ \begin{matrix} (B-A) \\ or \\ C \end{matrix} \right\} \times 100}{\text{sample (g.)}}$$

According to this method it can not be recognized that the coexisting ethyleneoxide gives interferences below about 12°C

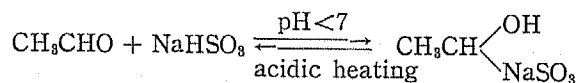**Example of an Experiment :** When a purified ethylenoxide completely released from acetaldehyde is titrated by this method after letting alone for 10, 30 and 60 minutes, $(B-A)$ as well as C are both zero in the error of experiment, namely in the neighborhood of this temperature there is no reaction between ethyleneoxide and $NaHSO_3$.

Ethyleneoxide reacts with $NaHSO_3$ at 60~70°C as the following:

$$CH_2 - CH_2 + NaHSO_3 \longrightarrow HO \cdot H_2C \cdot CH_2 \cdot SO_3Na$$
$$\diagdown O \diagup$$

sodium isoethionate
or β-hydroxyethanesulfonate

On passing ethyleneoxide into $NaHSO_3$ solution, the above reaction progresses quantitatively at 60~70°C. $NaHSO_3$ solution seems to be neutral in pH.

Acetaldehyde reacts with $NaHSO_3$ solution as the following:

$$CH_3CHO + NaHSO_3 \underset{\text{acidic heating}}{\overset{pH<7}{\rightleftharpoons}} CH_3CH \begin{matrix} OH \\ NaSO_3 \end{matrix}$$

This eaaction is utilized in order to refine the acetaldehyde.

Principle of Tomoda's Method: At pH<7, for pH of the ordinary water or distilled water are in this range, the above reaction has advanced to the right hand side.

Therefore, it is the essence of Ripper's method that, on adding $NaHSO_3$ excessively, the excess part is titrated by iodine solution. As a result of titration by iodine, HI and H_2SO_4 are produced and at the end of the titration pH becomes 2. After the correct titration by iodine with starch indicator, on adding $NaHCO_3$ until the undissolved one continues to present on the bottom, pH becomes 8 at which the above reaction shifts by several % to the left hand side. Therefore, if titrated immedeately after adding $NaHCO_3$ by the iodine normal solution, as $NaHSO_3$ which goes on to dissociate by several % is consumed by the titration, all $NaHSO_3$ which had been combined with CH_3CHO is thus gradually isolated and titrated completely. It is the Tomoda's method to use this titration value. The above volue of A is the one of iodine corresponding to $NaHSO_3$ which has remained without binding with CH_3CHO, and C is the value of iodine which had been combined exactly with CH_3CHO. If letting alone for a long time without titrating immediately after adding $NaHCO_3$, pH becomes near 9 and like a middle compound between CH_3CHO and S, which cannot be decomposed even by HNO_3 and Br_2, is produced, making an error by Tomoda's method. In the case of the quantitative analysis of the extremely small quantity, the error on titrating operation are negligible, for even the first significant figure is doubtful in this case. As things are said about aldehyde content in the synthesis of polyethyleneglycol, it is important to question how is the grade of aldehyde content. In this titrating method, on showing the aldehyde content by weight %, the content can be represented in the range of error within ± 10% by two significant figures up to the limit of inspection.

　　Tomoda's method is the one which uses the C in the above computation equation of acetaldehyde content, while Ripper's method uses the $(B-A)$ instead of C. The characteristic of the difference between Tomoda's one and Ripper's one consists in the fact that when the aldehyde content of 30 mg. is analyzed the latter gives almost always the higher values by 2 mg. than the former. It are experienced that the error in the operation of analysis can be guaranteed within 0.3 mg. for the treatment of 30 mg. of acetaldehyde. Ripper's method and Tomoda's one can be performed at the same time, requiring about one hour, while the colorimetry by the Schiff's reagent requires some 40 minutes.

Superiority between the Colorimetry and the Titration Method:
(1) As to the operation, the superiority can not be discussed between the both methods, however, the titration method is more general.
(2) As to the experimental values, the value from Tomoda's method can be used almost always with confidence, while in the case of Schiff's reagent method if the standard aldehyde solution is to be reliable and the interfernces of coexisting impurities in the reagent are missing or they are in a known magnitude, the value of the colorimetry seems to be correct.

Ponndorf's Method (Argentometry)

This method is the quantitative microanalysis of aldehyde and the one recom‑
mended by I. G. Ludwigshafen. Using $AgNO_3$, $MgSO_4$ and NaOH etc., after slow
redoxidation reaction, the solution is acidified in order to dissolve Ag_2O by H_2SO_4,
and removing metalic silver, then dissolved into nitric acid and titrated by the
Volhard procedure. This method carried is on quantitatively.

MANUFACTURE OF EMULPHOR–O 100% ACTIVE PASTE AND CATALYSIS OF
ETHYLENEOXIDE REACTION (Method of F. I. A. T. Final Report NO. 1141 pp, 59~60)

The author answered to Nippon Yusi Co limited about his question in regard to
the method of manufacturing on the addition polymerization of about 25 moles
ethyleneoxide to cetyl alcohol appeared in P. B. report as follows:

Example of Manufacturing: Putt sperm oil alcohol of 1, 130 lb. in a reaction
vessel, melt by heating and add 5. 7 lb. of NaOH to it. Heat to 120°C under
vacuum (about 100 mm. Hg) with stirring, keeping on with this procedure for one
hour. Subsequently cool it to 80°C and add 2($\frac{1}{3}$) quarts of water. Close the vessel
and pass nitrogen to remove air in it at least three times, finally set its gauge
pressure at 0. 3 atm. Heat the contents in the vessel to 150 ~ 160°C, and supply
liquid ethyleneoxide of 682 gallons to it by the pressure of 3 atm. of a supply‑tank
with stirring. The supply–velocity is about 25 ~ 50 gallons per hour. Hold the
reaction temperature at 150~160°C under the gauge pressure of 1. 5~2 atm. by
passing cooling water through a jaket.

The Questions from Nippon Yusi Co. :
(1) What object has the reduction of pressure? If it is considered to be a dehydra‑
ting operation, the later addition of water has no meaning.
(2) It is considered that if water is added in order to disperse the NaOH catalyst
in the system, it seems better for the sake of the effect of dispersion to add a
NaOH solution prepared beforehand. Then what a role has the addition of water ?

The Author's Answer: He considers the reduction of pressure as the operation
of dehydration. It is general for desiccation to use the temperature about 20~30°C
higher than the boiling point of the material to remove. In this case the stirring
can be used as the substitute for the capillary tube to make boiling. The object of
dehydration is perhaps to realize the equilibrium relation;

$$ROH + NaOH \longrightarrow RONa + H_2O,$$

as already mentioned, which is considered as the true form of the catalysis in the
ethyleneoxide polymerization at 120~130°C. In order to shift this relation to the
right hand side, the dehydration is necessary to perform. In the case of polyethyl‑
eneglycol the dehydration is naturally performed by the strong hygroscopic property
of surplus glycol merely by heating the glycol with NaOH added.

The later addition of water perhaps has no object to disperse the NaOH catalyst,
and on the contrary to the question the effect of dispersion should become worse in
the case in which NaOH is added as the aqueous solution, for sperm oil alcohol

can hardly mix well with water; it is the reason why the former can be distilled with steam. As the affinity between NaOH and water is so strong that, in the case of adding NaOH, pockets for NaOH aq. is produced in the system and NaOH embraced by H_2O can hardly be dispersed to catalyze the addition polymerization smoothly.

When water is added the equilibrium relation has already shifted to the right hand side and the RONa has been distributed extending through the system. Water added is the catalyst as the one contributing the above relation. The amount of it is of the extent which cannot permeate into the system for the sake of its insolubility in sperm oil alcohol, and hence it can not shift the relation completely to the left hand side. Superfluous water which is added after forming alcoholate assists for Na^+ ion to move about in the system in order to act as catalyst uniformly with all molecules of sperm oil alcohol; in due time the product of polymerization perhaps goes on to become familiarer with water molecules. On that occasion that molecules which are needed to the equilibrium relation acting as catalyst become easier to remain in the system in spite of high temperature such as 150~160°C under 1.5~2 atm. (gauge pressure).

EXPERIMENTS

Inpurities in crude Ethyleneoxide used :

ethyleneoxide   96.8% (Deckert's method ameliorated)

water   0.63 (Carl-Fischer's method)

dichloroethane   0.38 (decomposing by KOH)

acetaldehyde   0.35 (Tomoda's method)

ethylenechlorhydrine 0.04 (by the method from Analytical Chemistry *20*, 68 (1948))

CO_2 0.004

total   98.20%

One of the Experimental Facts

In imitation of P.B. report, add the solution of CH_3OH which contains CH_3ONa in the concentration of 10 % to polyentyleneglycol of M.W. 1540, and pass N_2 through the system to remove CH_3OH at 130°C for 15 minutes by using batch system with stirring. Then the velocity of absorption of ethyleneoxide appeared to be smaller than the case of NaOH catalyst.

The explanation of this fact is as follows ; for instance, water which should be a catalyst of plymerization for ethylene-oxide decreases the reaction velocity of ethyleneoxide when it is used too much; 109 g. of NaOH makes already a saturated solution along with 100 g. of water and by this water it loses its ability of dehydration. Therefore, so much quantiy of water with a little NaOH can keep colouring away from polyethyleneglycol, but on the contrary it decreases the rate of absorp-

tion of ethyleneoxide. CH_3OH is an organic solvent like water. The rate of polymerization on adding ethyleneoxide to methanol is perhaps small under Alkali catalyst in the same manner as the reaction between H_2O and ethyleneoxide. It is natural for the rate of reaction to be deceased for the sake of its so much amount remaining in the system, for it is insufficient to remove methanol completely by passing nitrogen through the system for 15 minutes at 130°C. In the synthesis of polyethyleneglycol there are quite opposite phenomena from the case of the best procedure, in spite of performance in the imitation of the so-called best method as seen in the colouring phenomena and the absorption rate of ethyleneoxide.

Another one of Experimental Facts

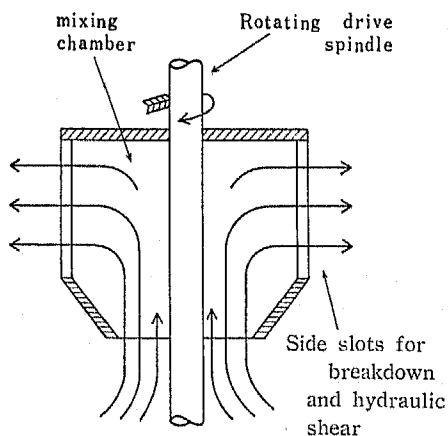In the case of the polymerization for polyethylenegoycol of M. W. 300, the following results were obtained ;
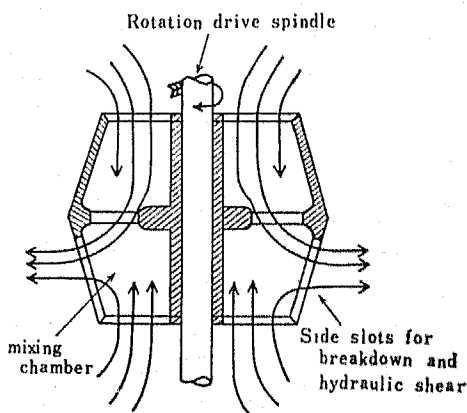

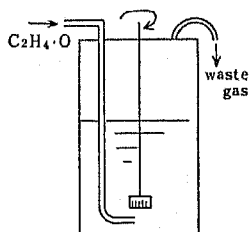Fig. 8   Dispersator (Simplex)

Fig. 9   Dispersator (Duplex)

Fig. 10
Vessel with dispersator.

(1) **The case of using a dispersator**[56];

When excessive quantity of ethyleneoxide in passing through the system was 0~5%, the total time for polymerization was required for 10 hours and the reaction temperature used was 130°C, where the quantity of NaOH catalyst was 26 % of glycol (whose quantity was 1 kg.). When, in another case, the excessive quantity of that was 17 %, the required time was 4 hours and 5 minutes, and in this case the reaction could not be controled by cooling and the temperature amounted to 151°C at the maximum, where the quantities of NaOH and glycol as well as other condition were the same as before. In both cases The polyethyleneglycol were coloured.

(2) **The case of spouting up of ethyleneoxide through glass filter** (see Fig. 2):

When the excessive quantity was 0~5 %, the total time was 6 hours at 130°C, where NaOH and glycol used were the same as the above. (glass filter NO. 4 was used). In this case **colourless product** was obtained.

Though it is anticipated that in the case of excessive passing by 20% of ethyleneoxide the reaction time will be required for 8.6 hours or so from the following three data, but the above fact shows that it is 4 hours or shorter.

% of excessive C_2H_4·O,	total C_2H_4·O, (moles)	spouting method,	dispersator method
3	5.6	6	10
20	6.5	5.2	(8.6)

The effect of dispersator for the polymerization of ethylene oxide is considered as follows : the above fact that the time required was 10 hours which is longer than the case of spouting method would be due to the inappropriate property of stirring for the inhomogeneous reaction between glycol and gaseous ethyleneoxide even with high ability of dispersator (see Fig. 11). On the contray, the fact that the above shorter time of the reaction, namely 4 hours or so, was required in the case of 17 % excess of ethyleneoxide would be due to the local heating resulted from the peculiarity

Fig. 11 Stirring with dispersator.

of dispersator together with the heat of polymerization, which is calculated as 22 kcal./mole from the heat of combustion of polyethyleneglycol, as well as the pressure effect by centrifugal force given by the strong rotation of dispersator.
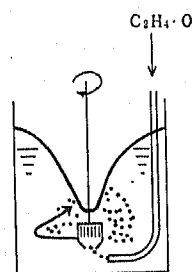
At all events in the case of using dispersator it is needed to take care of the colouring as well as the depolymerization due to the local heating or severe conditions and under certain circumstances by the material which makes the dispersator.

Refinement of Ethyleneoxide (Removement of Acetaldehyde)

In order to refine the ethyleneoxide, soda lime tower is used in a experiment of small scale, but there is a difficult matter to industrialize with it. Soda lime is a catalyst for polymerization whose strength is much weaker than NaOH and KOH.

The weak points of using soda lime are as follows: (1) It is difficult to remove from the tower in order to exchange it, for aldehyde resin sticks to it very tightly. (2) As the insides of tower cannot be seen, it is difficult to determine its decreasing degree of activity. (3) Soda lime removes aldehyde by polymerization of the latter; as the temperature rises by the heat of the polymerization its efficiency of the removement of aldehyde falls off so much, but it is difficult to cool the insides of the tower. The efficiency of the removement is higher at about 18°C and it falls as the temperature rises in a laboratory experiment (notice that the boiling point of acetaldehyde is about 20°C, while that of ethyleneoxide is about 10.7°C). When the temperature is the lower the loss of ethyleneoxide becomes the larger.

Prior to passing through the soda lime tower, it is needed to dry acetaldehyde sufficiently by CaO, otherwise acetaldehyde can not be removed. The efficiency of removement changes depending on the hygroscopicity.

Ameliorated Method to remove Acetaldehyde: It is good to use concentrated aqueous solution of NaOH (40 %) ; by this method acetaldehyde decreases to one tenth. According to experiences the concentration of acetaldehyde at the formation

$$\text{ethylenechlorhydrine} \begin{cases} \text{ethyleneoxide} \\ \text{acetaldehyde (small quantity)} \end{cases}$$
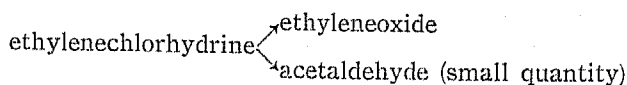
of ethyleneoxide from ethylenechlorhydrine is about 0.4~0.5%. Though passing ethyleneoxide through an aqueous solution of NaOH (40 %), it does not isomerize at room temperature. The moisture of ethyleneoxide after passing through it is not almost altered, therefore, it is sufficient to make ready the drying tower of CaO immediately after the exit.
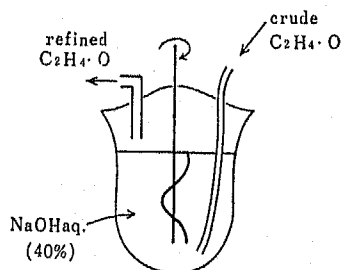

Fig. 12 Purification of $C_2H_4 \cdot O$ from $CH_3 \cdot CHO$.

The impurities of ethyleneoxide are removed by 4 towers of each 50 stairs in America; it is conjectured that the first tower will perhaps remove water, the second tower will remove dichlorethane, the third tower will remove materials of boiling points in the range 20~80°C, and the forth tower will remove acetaldehyde. Two towers of 102 stairs are also used for industrial uses in America, and by this arrangement aldehyde in ethyleneoxide falls below 0.1%. By the way, a tower can divides components into two parts only.

An Example of refining Processes of Ethyleneoxide by 40 % NaOH

When ethyleneoxide of 95 % (weight) is passed through NaOH aq. (40 %) in a rate of 50~60 l(liquid)/hr. at 30°C, the purity of ethyleneoxide is not changed in the experimental error, and the concentration of 0.9% of acetaldehyde falls to that of 0.3%; NaOH aq. is diluted by 3% and glycol increases by 2% (weight) in 30~40 hours. Total NaOH aq. used is about 250 l., the velocity of ethyleneoxide passing through NaOH aq. is 8.28 l./sec., the contact area of ethyleneoxide with NaOH aq. is 238 cm², the contact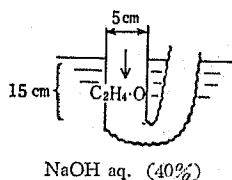 time between them is 0.037 sec., and the velocity of change from ethyleneoxide to glycol is 0.00684 mole (glycol)/sec. = 0.424 g./sec. (the volume of glycol is about 55.9 ml./mole at 1 atm., the volume of liquid ethyleneoxide is about 49.9 ml./mole). If roughly calculated the velocity constant "k" of ethyleneoxide to glycol is 4.34×10^{-4}:

$$\therefore 0.00684 \text{ mole/sec.} = k (15.78 - 0.00684) \text{ mole/sec.}$$

Fig. 13 Industrial refining of ethyleneoxide by NaOH aq. (40%)

Manufacturing Process of Polyethyleneglycol (in small scale until. M. W. 4000)

(1) Raw material

Distillation of Ethyleneoxide: ethyleneoxide in which the concentration of alde-hyde should be below 0.02 % is distilled through the soda lime tower with 0.2 ml./l. hr. of space velocity.

Distillation of Glycol: at 89±1°C (12.5 mm. Hg), reflux ratio is 1/10.

Preparation of CH_3ONa: methanol 322 g.; Na 46 g.; a quantity of methanol collected after the reaction is 246 g. (96%); the reaction temperature is 40°C.

Preparation of NaOH: let NaOH which is melted in a Ni or stainless crucible, flow on an iron plate and store it in a tightly plugged bottle. (decrease of weight is about 10 % at all)

(2) Quantity of Catalyst: use a quantity of NaOH so as to be 0.05 % of the last quantity at every step, but use CH_3ONa to be 0.1 % of the last quantity in the case of the reaction of M.W. 1540 → M.W. 4000.

(3) Liquid of Reaction: glycol and M.W. 300 of polyethyleneglycol are both liquid at room temperature. Polyethyleneglycol of M.W. 1540 is used after melting at 70°C.

Ethyleneoxide: it is treated at 8°C.

(4) Displacement of air in the reaction system by nitrogen with an aspirator for the prevention of explosion.

(5) Preliminary Heating of Reaction Tower: at 125~130°C.

(6) Cooling of the Cooler as well as the Collecting Tank of Ethyleneoxide withdrawn, at 5°C.

(7) Generator of Ethyleneoxide: heat it at 12~24°C. (messcylinder).

(8) Resistance of Spouting Plate, R: it is experienced as follows,

$$R(cm. Hg) = P - p - 0.077h$$

where P=supplying pressure, p=pressure of gas on the reacting liquid (cm. Hg), h=height of liquid (cm.), these are to be of values measured when one to three bubbling lines are rising into the liquid in the vessel. Therefore, the value of R is assumed to be a function of h (see Fig. 2).

(9) $\Delta H = P - p - h - R$ (cm. Hg): read mercuric manometers at each reaction and make (P-p), then ΔH is measured from the value h, and hence R. ΔH is used in order to control the polymerization reaction.

(10) Reading the graduation of generator of ethyleneoxide gas and the height of reacting liquid in the vessel for control of the reaction.

(11) The end point of the reaction is known by the height of reacting liquid on the whole and is tested by the measuring of the melting point picking up the sample by a capirally tube.

(12) Neutralization: it is performed by the quantity of calculated quantity of acid. If Alkali catalyst is used over the standard of ashes, neutralize the product by H_2SO_4 and filter. Neutralization by HCl is difficult to filter the product. Neutraliza-
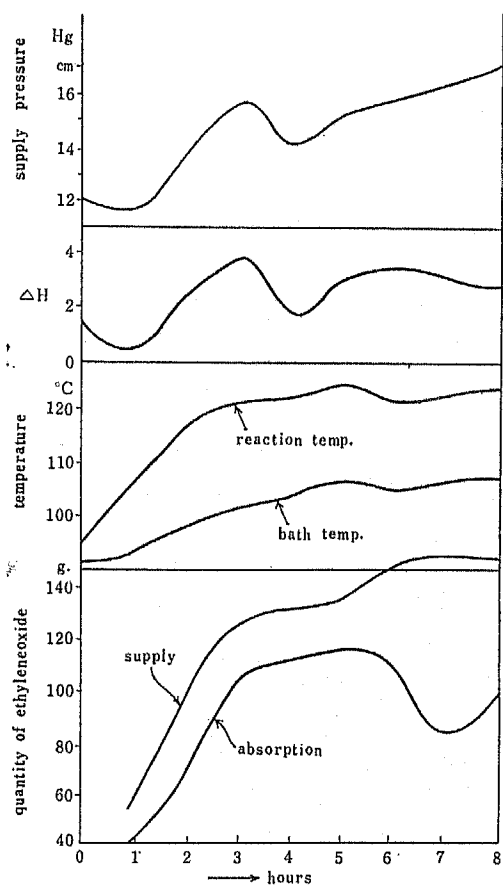
Fig. 14 Synthesis of polyethyleneglycol of
        M. W. 300 starting from glycol by
        NaOH catalyst.

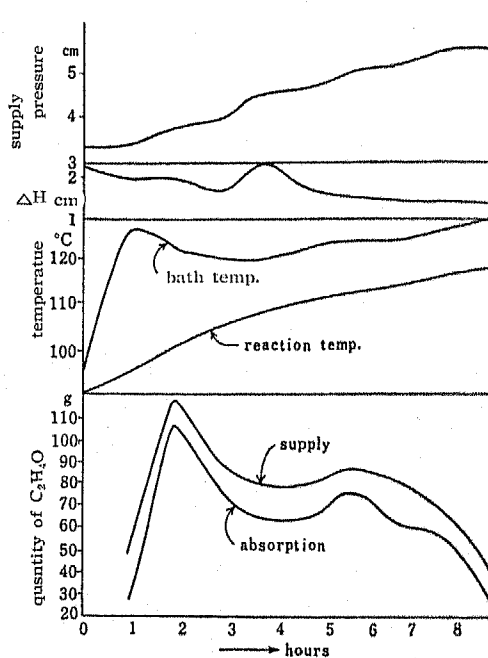
Fig. 15 Synthesis of polyethyleneglycol of
        M. W. 1540 starting from M. W. 300
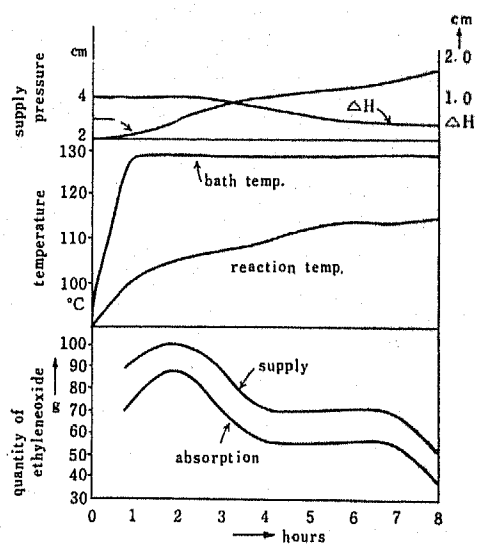   by NaOH catalyst.

Fig. 16 Synthesis of polyethyleneglycol
        M. W. 4000 starting from M. W. 1540
        by CH_3ONa catalyst.

tion by acetic acid remains a stench in the product, hence it cannot be used

Granted quntity of maximum ashes (weight %)

M. W.	200 ~ 600;	1000 ~ 1500;	1540;	4000;	6000
%	0. 10	0. 10	0. 10	0. 20	0. 20

A Device of Bearing Part of a Dispersator

If a dispersator with 3000~4000 r. p. m. is used for polymerization equipment, in order that no compressed C_2H_4O gas comes to that part rubbing against the bearing, which is the danger zone for explosion of C_2H_4O, by utilizing the centrifugal force of the dispersator a device of bearing part is considered as follows;

$$\text{Centrifugal force } F = \frac{m\pi^2 rn^2}{900} \text{ (kg.)}$$

where n=r. p. m., m= mass of oil or Hg, etc., and r=radius of disk. When, for example, r=3m., Hg=100g., a force F acting on the wall, "a" (Fig. 17), is F= 270 kg., then the centrifugal force per unit area at the disk periphery h (Fig. 18) is

$$\frac{F}{2\pi rh} \text{ (kg.)},$$

where h=width of disk periphery. If, for instance, the pressure of ethyleneoxide is 2kg./cm.^{2}, it is sufficient that the value of centrifugal force of oil etc. acting on the wall, a (Fig. 17), is much greater than that value, as C_2H_4O does not come in this case over a to the bearing part and does not contact with the heat of bearing. If the equipment like Fig. 19 is used, the strong points of spouting up method and of the stirring method by dispersator are both gratified, considering well as to the decolouring of the process for polymerization.
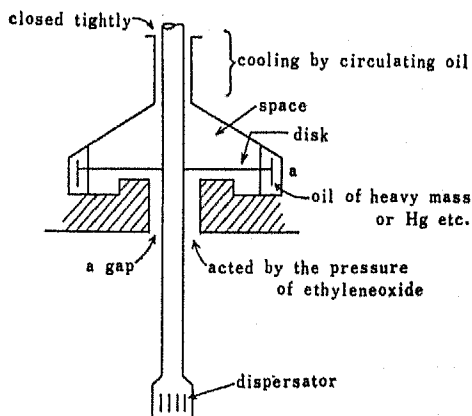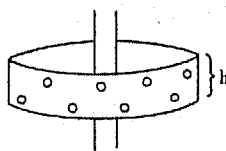

Fig. 17 Bearing part for safty from
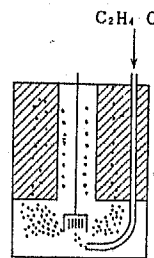   ethyieneoxide

Fig. 18
Disk in Fig. 17

Fig. 19

Table 3

An example aimed at the synthesis of **white colored** polyethyleneglycol

(by the method of spouting up through a glass filter).

Starting Materials			Reaction		Raw Products					
material	weight (g.)	catalyst	temp. (°C)	hrours	product (g.)	magnifica- tion	pH*	(sec.) Saybolt	colour	mark
glycol	200	NaOH 0.5g.	125~ 130°	7	985	4.9	10.1	41	colorless	M.W. 300
300	200	NaOH 0.6g.	〃	8	600	4.7	9.9	120	colorless	M.W. 1540
1540	200	CH₃ONa 2g.	〃	8	660	2.9	9.8	683	colorless	M.W. 4000

* values measured in 5% agueous solutions at 25°C.

Table 4 Physical Properties of Ethyleneglycol

Absorption spectra   Absorption maximum are approximately at 9547A, 9610A (—OH harmonic band) In comparison with monohydroxy aliphatic alcohols there is very weak absorption in this range, it is said that this will be due to the dissociation of glycol molecules. [57]

Raman spectra   See Hibber's work. [58]

Azeotropes   Azeotropes are not formed with H_2O, 1-Butanol, C_6H_6 Cyclohexame, Cyclohexanol and 1-Hexanol, the others generally form azeotropes.

Boiling point   197.6°C (760mm).

Density (true value)   1.11336 g./ml. (20°C)

Dielectric constant   38.66 e.s.u. (20°C, at 150 meters)

Dipole moment   2.20 ± 0.02×10¹⁸ e.s.u. (30°C)

Electric conductivity   1.07×10 mhos (25°C)

Entropy of formation   39.9 kcal./mole/°C[59] (25°C)

Free energy of formation   —80.2 kcal./mole. [59]

Freezing point   —13°C

Heat of combustion   —283.3 kcal./mole (at constant pressure, 20°C)

Heat of formation   —180.1 kcal./mole[60] (20°C)

Heat of fusion   44.7 kcal.

Heat of dissolution $C_2H_4 \cdot (OH)_2$ formed, 0.60 cal. /mole evolved. [61]

Heat of vaporization   191 cal./g. (760mm)

Molecular entropy   —105.4 kcal./°C[59].

Molecular volume   55.904ml. (25°C) 59.045ml. (105°C)

Molecular weight   62.07

Apparent spcific gravity   1.1155 (20°C/20°C)

Specific heat   0.561 cal./g./°C (20°C); s.h. = 0.538+0.00113t°

Total surface energy   74.52 ergs. (at b.p.)[62]

Surface tension   48.4 dynes/cm. (20°C); s.t. =50.21—0.089t°

Vapor pressure   0.06mm (20°C) ; log p=7.8808 $- \dfrac{1957}{193.8+t°}$ (100 to 1500mm)

Viscosity   20.93 c.p. (20°C)

Table 5　Physical properties of ethyleneoxide

Azeotropes　　reference[64]

Boiling point　　　10.7°C (760mm)[65]

Critycal pressure　　　1043 psia

Density (true value)　　　0.8697 g./ml.

Dielectric constant　　　13.9 e.s.u. (−10°C)[66]

Electric moment　　　1.88×10^{18} [67]

Entropy (total)　　　57.38 cal./°C/ml. (10.5°C, 760mm)[68]

Entropy (total)　　　57.94 cal./°C/ml. (25.0°C, 760mm)

Limit of explosion in the air ⎫　100% (volume)
Upper limit　　　　　　　　　⎬
Lower limit　　　　　　　　　⎭　　3% (volume)

Freezing point　　　−111.3°C

Heat of combustion　　　312.55 ± 0.20 kcal./g./mole[69] (25°C, 760mm)

Heat of formation (vapor)　　　17 kcal./g./mole[70]

Heat of formation (liquid)　　　23.3 kcal./g./mole.[70]

Heat of fusion　　　1236.4 col./mole.[68]

Heat of dissolution into water　　　1.5 kcal./mole[70] (constant pressure)

Heat of evaporation　　　245 Btu/lb.[65] (10.7°C, 760mm)

Heat of evaporation　　　6101 ± 6 cal./mole[68] (10.5°C, 760mm)

Heat of evaporation (total)　　　6082 cal./mole[68] (10.5°C, 760mm)

Temperature of combustion in the air　　　429°C[71] (760mm)

Melting point　　　−112.51°C[71]

Molecular heat　　　16.35 cal./°C/mole[74] (160.65°K, melting point)

　　　　　　　　　19.80 cal./°C/mole (− 〃 −)

Molecular volume　　　49.9[65] (10.7°C, 760mm)

Molecular weight　　　44.06

Valence angle of oxygen　　　77°[67]

Apparent specific gravity　　　0.8711[74] (20°C/20°C)

Specific heat　　　0.268 cal./g./°C[72] (34°C, 760mm)

Temperature of spontaneous combustion　　　571°C[73]

Vapor pressure　　　21.2 psia[74] (20°C) (1890mm Hg at 129.5°C)

Absolute viscosity　　　0.32 c.p.[65] (0°C)

Table 6   Physical Properties of Polyethyleneglycol for industrial Uses

Mark	mean molecular weight	range of freezing point °C	specific gravity 20/20°C	saybolt viscosity at 210°F	Solubility to H_2O at 20°C % by wt.	ignition point	relative degree of hygroscopicity (glycerol=100)	pH of aqueous solution (5%) at 25°C
Liquid Polyethyleneglycol								
200	190~210	super cool	1.12	38~42	perfect	340	70	4~7
300	285~315	−15~8	1.13	42~48	perfect	385	60	4~7
400	380~420	4~10	1.13	45~55	perfect	435	55	4~7
600	570~630	20~25	1.13	56~66	perfect	475	40	4~7
Solid Polyethyleneglycol "Carbowax"								
1000	950~1050	38~41		85~100	nearly 70	530	35	4~7
1500a	500~600	38~41	1.151b	70~90	73	430	35	4~7
1540	1300~1600	43~46	1.15	120~150	70	460	30	4~7
4000	3000~3700	53~56	1.204b	350~400	62	535		4.5~7.5
6000	6000~7500	60~63c		3200~4200	nearly 50	480		4.5~7.5

a = Equal weight mixture of polyethyleneglycol 300 and Carbowax compound 1540.

b = density g./cc (20°C)

c = range of m.p.

SUMMARY AND ADDENDUM

In this paper [I], a course of colouring as well as the device of decolouring about the polymerization process, the mechanism of polymerization catalysis, the optimum reaction temperature, and its manufacturing conditions etc. are discussed in detail in connection with polymerization reaction of ethyleneoxide, which is made via ethylenechrorhydrine, to polyethyleneglycol.

In the next place the author states in respect to "the synthesis of hexachloro-benzene from non-γ-B.H.C. for the manufacture of pentachlorophenol" and "the synthesis of ethyleneimine"; in the former hexachlorobenzene is synthesized from the decomposition of non-γ-B.H.C. by heat and the simultaneous chlorination of it in gaseous phase at 600°C, and in the latter ethyleneimine is produced along with the yield of 80.3% (purity of 97%) and of 84.2% (21.5%) from monoethanolamine.

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