Title: AN IMPROVED PROCESS FOR MANUFACTURE OF EPOXIDES, PARTICULARLY EPICHLOROHYDRIN

Abstract: A process for preparing epichlorohydrin comprising the following steps: reacting allyl chloride with an inorganic peroxide compound in the presence of at least one solvent at a temperature of about 35 to 75 degree C in a fixed bed column reactor containing a catalyst to obtain a resultant containing a mixture of epichlorohydrin, unreacted allyl chloride, solvent and water; diluting the mixture with water, wherein the mass ratio of water to the mixture is about 0.2 to 0.7, to obtain a diluted mixture; cooling the diluted mixture to about 5-15 degree C to obtain a cooled diluted mixture; separating phase and aqueous phase from the cooled diluted mixture; separating and recovering unreacted allyl chloride and epichlorohydrin individuallu from the organic phase by fractional distillation; and separating and recovering solvent and water individually from the aqueous phase by fractional distillation.
AN IMPROVED PROCESS FOR MANUFACTURE OF EPOXIDES, PARTICULARLY EPICHLOROHYDRIN

Field of the invention:
This invention relates to an improved process for the manufacture of epoxides, particularly epichlorohydrin.

More particularly, this invention relates to a process for manufacturing of epichlorohydrin from allyl Chloride.

Background and prior art
The largest use of Epichlorohydrin is in the manufacture of Epoxy Resins, which find applications in surface coatings. A number of surface active agents are also being made from Epichlorohydrin which is used as detergents, demulsifiers and the like. Epichlorohydrin also finds applications in the preparation of a number of pharmaceuticals, textile conditioners and dyes, paper sizing agents and the like. It is used as a solvent (e.g. for cellulose acetate) as a stabilizer for polyvinyl chloride, chlorinated rubbers and several chlorine containing insecticides, and as an additive to lubricating oil greases.

Over the last several decades, different types of manufacturing processes have been developed for transforming olefins such as allyl chloride to epoxides such as epichlorohydrin using active oxygen species and inorganic salts. Conventionally allyl chloride in excess is epoxidized with a solution of per acetic acid to form Epichlorohydrin. The excess allyl chloride and epichlorohydrin formed are separated by distillation. The main disadvantage of the above conventional process is that the complete separation of acetic acid from the epichlorohydrin-reaction mixture is
possible only with the expenditure of great costs because of closely situated boiling points of acetic acid (117.5 degree C) and that of epichlorohydrin (116 degree C). In an another method, Propylene is reacted with acetic acid in presence of Palladium catalyst and Oxygen gas to give ether, which on chlorination in presence of COCl₂ and organic solvent gives mixture of 2,3-dichloroisomer and 1,2-dichloroisomer. This on addition of water gives mixture of 1,2-dichloropropanol and 2,3-dichloropropanol, further addition of calcium hydroxide gives epichlorohydrin. However, in the chlorination step, the COCl₂ catalyst is required to be separated after the reaction. In addition, the yield of product is not high (e.g. 47.5% - 84.2%) and therefore the un-reacted Allyl chloride, is required to be separated and recovered. In one more method, propylene is reacted with acetic acid in presence of palladium (Pd) catalyst in presence of oxygen gas to give ether. Ether is reacted with hydrogen chloride in presence of CuCl or FeCl₂ and aslo in presence of organic solvent to give Allyl chloride and acetic acid. This allyl chloride on hypo chlorination with Cl₂/H₂O gives mixture of 2, 3-dichloropropanol and 1, 2-dichloropropanol which on reaction with base as calcium hydroxide gives epichlorohydrin. The main disadvantage of these processes is that the reaction of addition of hydrogen chloride is carried in presence of CuCl or FeCl₂ catalyst which is a non-aqueous system to prevent hydrolysis.

Epichlorohydrin is industrially manufactured by chlorination of Allyl chloride, which is obtained, by high-temperature chlorination of propylene. By-products of chlorination are cis- and trans-1,3-dichloropropene and 1,2-dichloropropane. Glycerol dichlorohydrin are made from Allyl chloride with 1, 2, 3-trichloropropane being the by-product. Finally, Epichlorohydrin is produced from the glycerol-
dichlorohydrin mixture by treatment with base. The main disadvantages are,
1) The process uses lime/CaO, water and extra chlorine, resulting into high cost.
2) Expenses on the utilities involving steam, electricity, cooling water and air/N2 are very high.
3) Generation of effluents, which are of the order of 15-20 tons per ton of ECH product, is major problem in terms of operation cost and the statutory requirements.

The US Patent no. 6720435, 6288248 & 6350888 disclose a process for manufacturing of epichlorohydrin by reaction of allyl chloride with a peroxide compound in the presence of water, a catalyst and a solvent followed by a liquid-liquid extraction to separate the epichlorohydrin formed. The main drawbacks are, use of catalyst in powder form which reduces the rate of filtration, use of another chlorinated compound for the liquid-liquid extraction thereby increasing its recovery cost and quantity of aqueous effluents generated resulting into the increase in disposal and treatment cost.

US Patent no. 6380407 discloses a process for the manufacturing of an epoxide, in which an olefin is reacted with a peroxide compound in the presence of a zeolite-based catalyst and in the presence of a solvent in a reactor in the liquid phase. Gaseous compound is introduced continuously into the reactor at a flow rate which is sufficient to entrain at least some of the epoxide produced, which is recovered along with the gaseous compound at the point at which it leaves the reactor. Some of the draw backs are use of gaseous compound for carrying out the reaction which
results in consumption of extra energy in preheating the compound and also for maintaining the fluidization of the solid catalyst.

US Patent numbers 6677467, 6723861, & 6838571 disclose processes for manufacturing oxirane by reaction of an olefin with a peroxide compound in the presence of a catalyst and a solvent in series of reactor, each of which contains a portion of catalyst, in which the peroxide compound is introduced only into the first reactor of the series and the subsequent reactor(s) not being fed with fresh peroxide compound, but only with the peroxide compound which is present in the medium obtained from the preceding reactor and which was not consumed in this preceding reactor.

US Patent numbers 6720435, 6288248 & 6350888 disclose processes for a liquid-liquid extraction wherein, a chlorinated compound is used for the selective extraction of epichlorohydrin from the mixture of allyl chloride, methanol, water and epichlorohydrin. The extract phase contains only 10% of the epichlorohydrin produced whereas remaining 90% is in the aqueous phase. The isolation of epichlorohydrin from such an aqueous phase is a grey area where no work has been reported so far.

Hence there is a need for an improved process for the manufacture of epichlorohydrin in which minimum epichlorohydrin is lost into the aqueous layer and to increase the percentage yield by cascade reactions. The objects of the present invention address such needs.

**Objects of the invention**

One of the objects of the present invention is primarily directed to improve the overall epichlorohydrin product yield in the said process.
Another object of the present invention is to separate reactor product mixture into a mixture containing unconverted allyl chloride and methanol, which is fit for the recycle.

Yet another object of the present invention is to use allyl chloride for recovering epichlorohydrin from aqueous phase.

Yet another object of the present invention is to separate water, which is fit for recycle.

Yet another object of the present invention is to reduce the generation of effluents substantially.

Yet another object of the present invention is to improve the concentration of epichlorohydrin in the organic phase and to reduce the concentration of epichlorohydrin in aqueous phase as low as possible.

Yet another object of the present invention is to provide a cost effective process for the production of Epichlorohydrin from Allyl Chloride.

**According to this invention there is provided a** process for preparing epichlorohydrin comprising the following steps:

reacting allyl chloride with an inorganic peroxide compound in the presence of at least one solvent at a temperature of about 35 to 75 degree C in a fixed bed column reactor containing a catalyst to obtain a resultant containing a mixture of epichlorohydrin, unreacted allyl chloride, solvent and water; diluting the mixture with water, wherein the mass ratio of water to the mixture is about 0.2 to 0.7, to obtain a diluted mixture;
cooling the diluted mixture to about 5-15 degree C to obtain a cooled diluted mixture;
separating organic phase and aqueous phase from the cooled diluted mixture;
separating and recovering unreacted allyl chloride and epichlorohydrin individually from the organic phase by fractional distillation; and
separating and recovering solvent and water individually from the aqueous phase by fractional distillation.

**Brief Description of the Drawings:**
The invention will now be described with reference to accompanying drawings in which,
FIG 1: represents the schematic diagram for the process of the present invention;
FIG 2: represent the flow diagram of an extractor involved in the said process of the present invention as shown in FIG 1; and
FIG 3: represents the schematic diagram of the jacketed tubular reactor for one of the alternative embodiment of the present invention.

**Detailed description of the invention:**
Referring to the drawings particularly FIG 1

In accordance with this invention there is envisaged an improved method for production of epichlorohydrin by the catalytic oxidation of allyl chloride in jacketed tubular reactors (R1 and R2) containing packed catalyst. Inlet stream (IS) containing the reactants, allyl chloride, methanol and one part of fresh hydrogen peroxide is continuously passed
upward through the reactor (Rl). The stream at the exit of (Rl) containing the reactants along with 3-5 mole % of epichlorohydrin formed is mixed with second part of fresh hydrogen Peroxide and fed into the second Reactor (R2) for an efficient utilization of the catalyst activity and high percentage conversion of the reactants. Alternatively After the completion of reaction, an outlet stream (OS) from the reactor (R2), containing 7-9mole % of epichlorohydrin, unreacted allyl chloride, methanol and water at around 45-50 degree C is transferred to a holding tank (Tl). The effluent stream (ES) from the holding tank (Tl) is then mixed with process water (PW) from a tank (T2) and then fed to an extraction chamber (EC1). Typically, the extraction chamber (EC1 and EC2) consists of three separate units: a mixer (M), a cold extractor (CE) and a Decanter settler (DS), wherein the streams from the tank (Tl) and (T2) are thoroughly mixed in mixer (M) and then down streamed to a coil type cold extractor (CE) in which the reactor effluent and the process water from the mixer is led through the coil and coolant is circulated in the shell to bring down the temperature of the mixture in the coil. From the cold extractor the mixture of the reactor effluent and the process water is led to the decanter settler (DS) operatively placed below the cold extractor (CE) in the extraction chamber (EC), where a low temperature is maintained. In the decanter settler (DS) separation of the organic and the aqueous phase takes place by difference in densities of the two phases. The organic phase settles to the bottom of the decanter settler (DS) and is extracted through the outlet of the decanter settler (DS) through organic outlet. The aqueous phase is let off from the aqueous outlet of the decanter settler (DS). Further the aqueous phase comprising mainly water and methanol with some quantities of unreacted allyl chloride and some traces of epichlorohydrin is fed to an extraction chamber (EC2) for second time extraction of epichlorohydrin by addition
of allyl chloride. The organic phase (OP) and aqueous phase (AP) are separated in the extraction chamber. The AP from the (EC2) is passed into a fractionating column (Cl) to recover allyl chloride and methanol. The (OP) from the (EC1) and (EC2) is passed into the fractionating column (C2) to obtain crude epichlorohydrin with heavies which is further fractionated in column (C3) to obtain pure epichlorohydrin. The recovered allyl chloride and methanol from the column (Cl) and (C2) is recycled and mixed with the inlet stream (IS) of the reactor (R1) and water recovered from (Cl) is fed to the water tank (T2) and inlet of Cold extraction unit.

Typically, the mole ratio of reactants allyl chloride: peroxide fed to the reactor is as low as 1.0:1.0; the process also operates with 1.1-6.0:1.0 mole ratio with minor modifications.

Typically, the reaction is carried out at temperatures ranging from 35 to 75 degree C.

Typically, the intermediate stream coming out of the second reactor is maintained at 5-15 degree C for optimal results.

Typically, the mass flow rate of ES/PW is maintained in the range of 0.2 to 0.7.

Typically, the residence time of the mixture in the extractor ranges between 45 to 150 minutes.

Typically, the difference in specific gravity of settler liquids is maintained between 0.2-0.70 g per ml for optimal results.
Typically, the Epichlorohydrin so obtained is 99.9 % pure, free from other volatile impurities like methyl glycidyl ether or 2-methoxy-l-propanol or any other chloro-compounds.

Typically, the yield of epichlorohydrin based on hydrogen peroxide across the reactor is 97.1 % and across the extraction is 98.1 % and based on allyl chloride, the process yield is 95.1 %.

Description of figure 1:
In accordance with the present invention, figure 1 discloses one of the embodiments where in, the catalytic oxidation of allyl chloride takes place in jacketed (J) tubular reactors (R1 and R2) containing packed catalyst. Inlet stream (IS) containing the reactants, allyl chloride (ALC), methanol (MeOH) and one part of fresh hydrogen peroxide (HP) is passed into the reactor R1, and the second part of fresh Hydrogen Peroxide is passed into the second Reactor (R2). After the completion of reaction, an outlet stream (OS) from the reactor R2, containing epichlorohydrin (ECH), unreacted allyl chloride, methanol and water is transferred to a holding tank (T1). The effluent stream (ES) from the holding tank T1 is then mixed with process water (PW) and then fed to an extraction chamber (ECl). The organic phase (OP) and aqueous phase (AP) get separated in the extraction chamber (ECl). The aqueous phase (AP) from the ECl is passed into the EC2, in which second time extraction of ECH takes place by adding ALC to the extraction chamber EC2. The OP from the ECl and EC2 is passed into the column C2, however the AP from the EC2 is passed into the C1. The recovered ALC, MeOH from the C1 and C2 and process water from C1 are recycled and reused. The crude ECH obtained from the C2 is fed to a C3 to obtain pure ECH and heavies. The mass flow rate of ES/PW is maintained in the
range of 0.2 to 0.7. Typically the extraction chambers (EC1 and EC2) consist of three separate units: a premixer (M), a cold extractor (CE) and a Decanter settler (DS) as shown in Figure 2.

The premixer M is a preferred embodiment for proper mixing of two streams. The premixer M comprises glass beads wherein streams from T1 and T2 are thoroughly mixed before flowing downstream to a cold extractor CE. The cold extractor (CE) is a coil type of cooler in which the reactor effluent is led through the coil and coolant is circulated through the coolant inlet (IC) in the shell to bring down the temperature of the mixture in the coil to between 5 to 15 degree C and exits at the outlet (OC). The residence time of the mixture in the extractor ranges between 45 to 150 minutes. From the cold extractor the mixture of the reactor effluent and the process water is led to the decanter settler (DS) placed below the cold extractor (CE) in the extraction chamber EC, where the temperature of the mixture is maintained to around 5 to 15 degree C. The separation of organic and aqueous phase takes place by difference in densities of the two phases, in which the organic phase settles to the bottom of the decanter settler (DS) and is extracted through the outlet of the decanter settler (DS) through organic outlet. The resident time of the split phase content and the levels of the two phases are carefully controlled. The aqueous phase is let off from the aqueous outlet of the decanter settler (DS). The organic phase and the aqueous phase are collected from their respective outlet by siphon. The aqueous phase after the EC2 typically consists of mainly water and methanol with some quantities of unreacted allyl chloride and some traces of ECH. The organic phases obtained from the column C1 and C2 typically consists of epichlorohydrin, unreacted allyl chloride, and Methanol with some traces of water. The organic phase is led to the column (C2) where the crude
epichlorohydrin is obtained and is led to the column (C3) to obtain high purity epichlorohydrin as a side product. The recovered ALC and MeOH from the column C1 and C2 is recycled and mixed with the inlet stream (IS) of the reactor (R1). The aqueous stream is led to the column (C1) where essentially, methanol and allyl chloride and water get separated. The recovered ALC, MeOH and water from column C1 is sent back to the inlet of Reactor R1 and to the inlet of cold Extraction unit respectively.

Alternatively, as shown in the FIG: 3 the effluent stream from the reactor R2 can be recirculated several times in the same reactor by suitably adjusting the feed ratio that is hydrogen peroxide to allyl chloride.

This method of industrial manufacturing of the Epichlorohydrin from Allyl Chloride is more cost effective. Use of catalyst in the extrudates form reduces its cost of recovery and regeneration. Thus the operating cost in terms of the recovery of unconverted Allyl Chloride is reduced considerably. The production method of the present this invention reduces the consumption of utility steam on an overall basis compared to that being practiced industrially as the best. Thus, reduces the operating cost per unit weight of production of Epichlorohydrin, increases the overall yield of product epichlorohydrin and also improves the stability of all the downstream unit operations owing to less concentration of ECH in the aqueous phase. Thus in the method of this invention, as compared to the usual methods, high quality product is obtained in relatively high yield at comparatively lower operating cost of production.
The method disclosed by this invention gives quality product Epichlorohydrin at lower operating cost. The main advantages of the present invention are:

1. This method permits the epoxidation reaction of the allyl chloride to be carried out in fixed bed of catalyst using a split flow of peroxide component.

2. Being an exothermic reaction, the temperature rise across catalyst bed is effectively controlled by using excess of allyl chloride.

3. Excess Allyl Chloride & Methanol are recovered and are reused in the process, thereby reducing the unit consumption of raw materials.

4. Process water is recovered, recycled and reused in the cold extraction operation, thereby reducing the unit consumption of process water.

5. The quantity of solid effluent is nil as well as liquid effluent is negligible, thus reduces the cost of disposal.

6. The method covered by this invention reduces the total operating cost of the production of Epichlorohydrin from allyl chloride.

Thus with this method, high quality Epichlorohydrin product can be easily manufactured economically in a reasonably high yields and thus represents a new method for the continuous production of Epichlorohydrin from Allyl Chloride using a split flow of peroxide component suitable for industrial scale of application.
The invention will now be described with respect to the following examples which do not limit the invention in any way and only exemplify the invention.

Example 1:
Combined feed at a rate of 60 gms/hr containing excess AHyl chloride is reacted with one part of Hydrogen Peroxide in presence of Methanol as a solvent using 15 gms of TS-I catalyst packed in first reactor, which is a fixed bed jacketed tubular reactor, on a continuous basis to produce Epichlorohydrin. The stream at the exit of first reactor contains Allyl chloride (32.36 mole%), Methanol (52.05 mole%), Epichlorohydrin (3.97 mole%), & Water (11.57 mole%), which is mixed with the second part of Hydrogen Peroxide and is fed into the second reactor, which is also a fixed bed tubular jacketed reactor, containing 15 gms of catalyst on a continuous basis to produce Epichlorohydrin. The stream at the exit of second reactor contains Allyl chloride (25.39 mole %), Methanol (46.11 mole %), Epichlorohydrin (7.54 mole %), & Water (20.91 mole %). The second reactor effluent at a rate of 46 gms/hr is mixed with DM water in specially designed extractor equipment before chilled to 5 degree C. The weight ratio between process stream and water is maintained at 0.4. After having provided sufficient residence time of 100 minutes, two clear phases are separated. The bottom or organic layer is withdrawn at a rate of 28.09 gms/hr and contains Allyl chloride (59.80 mole %), Methanol (11.51 mole %), Epichlorohydrin (24.68 mole%), & Water (4.00 mole%). Finally, the top or aqueous layer is further extracted with fresh quantity of ALC at 50C so as to collect 9.02 gms/hr of Epichlorohydrin (Yield = 96.45%).
Example 2

Combined feed at a rate of 2100 gms/hr containing excess Allyl chloride is reacted with one part of Hydrogen Peroxide in presence of Methanol as a solvent using 800 gms of TS-I catalyst packed in first reactor, which is a fixed bed jacketed tubular reactor, on a continuous basis to produce Epichlorohydrin. The stream at the exit of first reactor contains Allyl chloride (35.36 mole%), Methanol (45.87 mole%), Epichlorohydrin (4.25 mole%), & Water (14.48 mole%), which is mixed with the second part of Hydrogen Peroxide and is fed into the second reactor, which is also a fixed bed tubular jacketed reactor, containing 800 gms of catalyst on a continuous basis to produce Epichlorohydrin. The stream at the exit of second reactor contains Allyl chloride (26.17 mole%), Methanol (46.16 mole%), Epichlorohydrin (8.06 mole%), & Water (19.57 mole%). The second reactor effluent at a rate of 2020 gms/hr is mixed with DM water in specially designed extractor equipment before chilled to 5 degree C. The weight ratio between process stream and water is maintained at 0.4. After having provided sufficient residence time of 100 minutes, two clear phases are separated. The bottom or organic layer is withdrawn at a rate of 1233.52 gms/hr and contains Allyl chloride (62.39 mole %), Methanol (14.25 mole%), Epichlorohydrin (19.93 mole%), & Water (3.42 mole%). Finally, the top or aqueous layer is further extracted with fresh quantity of ALC at 50C so as to collect 331.73 gms/hr of Epichlorohydrin (Yield = 96.69%).

While considerable emphasis has been placed herein on the steps and reactant chemical compounds of the preferred embodiments, it will be appreciated that many permutations and combinations of the process steps and the composition can be made and that many changes can be made in the preferred scheme without departing from the principles of the
invention. These and other changes in the preferred process steps as well as other steps of the process of the invention will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the invention and not as a limitation.
Claims:

1. A process for preparing epichlorohydrin comprising the following steps:
   reacting allyl chloride with an inorganic peroxide compound in the presence of at least one solvent at a temperature of about 35 to 75 degree C in a fixed bed column reactor containing a catalyst to obtain a resultant containing a mixture of epichlorohydrin, unreacted allyl chloride, solvent and water;
   diluting the mixture with water, wherein the mass ratio of water to the mixture is about 0.2 to 0.7, to obtain a diluted mixture;
   cooling the diluted mixture to about 5-15 degree C to obtain a cooled diluted mixture;
   separating organic phase and aqueous phase from the cooled diluted mixture;
   separating and recovering unreacted allyl chloride and epichlorohydrin individually from the organic phase by fractional distillation; and
   separating and recovering solvent and water individually from the aqueous phase by fractional distillation.

2. A process as claimed in Claim 1, wherein the inorganic peroxide is at least one peroxide selected from a group consisting of acetone triperoxide, hexamethylene triperoxide diamine, sodium peroxide,
barium peroxide, calcium peroxide, strontium peroxide, carbamide peroxide, magnesium peroxide and benzoyl peroxide.

3. A process as claimed in Claim 1, wherein the solvent is at least one solvent selected from a group consisting of methanol, ethanol, 1-propanol, 1-butanol, acetic acid and acetone.

4. A process as claimed in Claim 1, further comprising a step of recycling the recovered unreacted allyl chloride to the fixed bed column reactor in the process.

5. A process as claimed in Claim 1, further comprising a step of recycling the recovered solvent, to the fixed bed column reactor in the process.

6. A process as claimed in Claim 1, further comprising a step of recycling the recovered water for dilution.
FIGURE 1
FIGURE 3