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(54) Title: PROCESS FOR THE CATALYTIC HALOGENATION OF A HYDROXYLATED ORGANIC COMPOUND

(57) Abstract: The present invention relates to a process for the catalytic halogenation of an organic compound comprising at least one aliphatic hydroxyl group which comprises the step of contacting the organic compound comprising at least one aliphatic hydroxyl group with a hydrogen halide in the presence of a catalyst which is an organic polymer which comprises at least one carbonyl group, has a vapour pressure at the reaction temperature of less than 1 mbar, has a weight average molecular weight M_w of 500 g/mole or more, and is soluble in the reaction mixture at the reaction temperature.



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PROCESS FOR THE CATALYTIC HALOGENATION OF A HYDROXYLATED ORGANIC COMPOUND

The present invention relates to a process for the catalytic halogenation of an
5 organic compound comprising at least one aliphatic hydroxyl group by a
hydrogen halide in the presence of a suitable catalyst.

WO 2005/021476 describes a method of preparing the dichloropropanols 1,3-
dichloro-2-propanol and 2,3-dichloro-1-propanol by chlorination of glycerol
10 and/or monochloropropanediols with gaseous hydrogen chloride with catalysis
of a carboxylic acid, wherein the hydrochlorination is carried out in at least one
continuous reaction zone at reaction temperatures in the range of 70-140°C and
with continuous removing of the water of reaction, the liquid feed containing at
least 50% by weight of glycerol and/or monochloropropanediols. The carboxylic
15 acid preferably is acetic acid.

WO 2005/054167 discloses a process for producing dichloropropanol from
glycerol wherein the glycerol is subjected to a reaction with a chlorinating agent,
with the exception of a batch reaction carried out in the presence of acetic acid
or its derivatives as the catalyst. As the chlorinating agent preferably
20 substantially anhydrous hydrogen chloride is used. The catalyst preferably is a
carboxylic acid or a derivative thereof. The carboxylic acid in the catalyst
generally comprises from 1 to 20 carbon atoms. As particularly preferred
catalysts are mentioned acetic acid, formic acid, propionic acid, butyric acid,
fatty acids, and aromatic carboxylic acids such as benzoic acid.

25 WO 2006/020234 discloses a process for converting a multihydroxylated
aliphatic hydrocarbon or ester thereof to a chlorohydrin, wherein in a first step a
multihydroxylated hydrocarbon or ester thereof is contacted with a source of a
superatmospheric partial pressure of hydrogen chloride for a sufficient time and
at a sufficient temperature, and wherein such contacting step is carried out
30 without substantial removal of water. If a catalyst is used in this process, it may
for example be a carboxylic acid, an anhydride, an acid chloride, an ester, a

lactone, a lactam, an amide, a metal organic compound such as sodium acetate, or a combination thereof.

Problems associated with the use of the above-mentioned types of catalysts are
5 that these catalysts are all organic compounds with a low molecular weight. These compounds are relatively volatile. This has the effect that when the chlorinated product is drawn off by evaporation, not only traces of the catalyst will end up in the product, but also intermediate products and byproducts, for example esters of the catalyst with the alcoholic starting material, may end up in
10 the halogenated product. This may result in a large number of undesired impurities in the reaction product that need to be removed in additional purification steps or impurity destruction steps. Furthermore, this results in significant catalyst loss.

15 WO2006/020234 furthermore discloses that a solid catalyst may be employed which has the advantage that it can be retained within the process equipment by means of a filter or equivalent device.

However, a disadvantage of a solid catalyst is that the reactant needs to adsorb onto the catalyst surface area to form an intermediate which is subsequently
20 halogenated. Inherent to this process, only the surface of the solid catalyst is effectively used. Furthermore, both adsorption kinetics and mass transfer limitation for transport of the organic reactant and the hydrogen halide to the catalyst surface will slow down the conversion rate.

25 It is an object of the present invention to provide an improved process wherein the above-mentioned problems are overcome.

It has surprisingly been found that this objective is met if the organic compound comprising at least one aliphatic hydroxyl group is contacted with a hydrogen
30 halide in the presence of a particular polymeric catalyst. In more detail, the present invention relates to a process for the catalytic halogenation of an organic compound comprising at least one aliphatic hydroxyl group which

comprises the step of contacting the organic compound comprising at least one aliphatic hydroxyl group with a hydrogen halide in the presence of a catalyst, wherein the catalyst is an organic polymer comprising at least one carbonyl group, having a vapour pressure at the reaction temperature of less than 1
5 mbar, having a weight average molecular weight M_w of 500 g/mole or more, and which is soluble in the reaction mixture at the reaction temperature.

The performance of a specific, polymeric, catalyst according to the present invention in the halogenation reaction of a specific organic compound
10 comprising at least one aliphatic hydroxyl group can easily be determined and verified using the following test method.

In a 500 ml flask, 1 mole of the organic compound to be halogenated is mixed with 0.1 mole of the polymeric catalyst. The flask is placed in an oil bath and the reaction mixture is heated to a temperature that approximately equals the
15 boiling point of the main halogenated product which will be formed. The flask is fitted with a two-holed stopper which carries a long tube reaching to the bottom of the flask and a short exit tube. The long tube is connected to a hydrogen halide generator. The short one is connected to a catch bottle and some system for absorbing any excess of hydrogen halide. A stream of dry hydrogen halide is
20 passed into the mixture. The absorption of gas is rapid at the start but gradually falls off towards the end of the reaction. Hence, the stream of hydrogen halide should be regulated accordingly. After 24 hours, the reaction is terminated and the reaction mixture is analyzed using HPLC.

The performance of the polymeric catalyst is considered to be acceptable if at
25 least 30% conversion of the organic compound is observed after 24 hours.

An advantage of the present invention is that application of a polymeric catalyst according to the present invention takes away the adsorption inhibition and most of the mass transfer limitation issues that occur when a solid catalyst is
30 applied. Since the catalyst according to the present invention is dissolved in the reaction mixture, the total catalyst mass is effectively used. Furthermore,

because of its advantageous vapour pressure properties, the risk of finding traces of this catalyst in the isolated halogenated product is minimized.

5 Carbonyl groups, which can be present in the polymeric catalyst in the form of an aldehyde, a ketone, a carboxylic acid, an ester, an amide, an enone, or a carboxylic anhydride group, can be present in the polymeric backbone and/or in one or more side-chains. Preferably, the organic polymeric catalyst comprises at least five carbonyl groups, which are preferably present in the form of a carboxylic acid, an ester, or an amide.

10

Preferably, the polymeric catalyst has a branched structure. The term "branched structure" means that the polymeric backbone of the catalyst comprises at least one side-chain, *i.e.* a series of carbon atoms directly connected by chemical bonds to said polymeric backbone. The side-chains are hydrocarbon chains comprising one or more carbon atoms, which may be aliphatic or aromatic in nature and which are optionally functionalized, for example with sulphate groups, sulphonate groups, carboxyl groups, hydroxyl groups, phosphate groups, phosphonate groups, phosphino groups, or combinations thereof. The irregularity of the polymeric structure has the advantageous effect that the solubility of the catalyst increases. Hence, it is preferred that these side-chains are also branched.

25 As mentioned above, the polymeric catalyst according to the present invention has a weight average molecular weight of 500 g/mole or more. Preferably, it has a weight average molecular weight of at least 650 g/mole, more preferably of at least 800 g/mole. The weight average molecular weight preferably is less than 50,000 g/mole, more preferably less than 40,000 g/mole, even more preferably less than 25,000 g/mole, and most preferably less than 15,000 g/mole.

30 As used herein, the term "soluble in the reaction mixture" means that the polymeric catalyst is capable of being essentially uniformly blended and/or molecularly or ionically dispersed in the reaction mixture at the reaction

temperature to form a true solution (analogously to *Hawley's Condensed Chemical Dictionary*, 11th Edition, revised by N.I. Sax and R.J. Lewis, Sr, Van Nostrand Reinhold Company Inc., New York, at page 940). It is noted that the term "soluble in the reaction mixture" also includes the formation of vesicles or micelles.

Preferably, the polymeric catalyst according to the present invention is a dendritic polymer or an organic flocculant.

The term dendritic polymer according to the present invention is meant to denote every compound which has a regular or irregular dendrimeric structure, and, more particularly, is either a dendrimer in which well-defined branches radiate from a central core becoming more branched as they extend to the periphery, or a hyper-branched polymer irregularly branched with branches not emanating from a central core.

An organic flocculant is a substance that induces flocculation, *i.e.* it combines or aggregates with suspended colloidal matter, particularly in such a way that they form small clumps or tufts. An example of an organic flocculant is a polyelectrolyte, *i.e.* a polymer the repeating units of which bear an electrolyte group which will dissociate in aqueous solutions, making the polymer charged. Suitable flocculants can have a weight average molecular weight up to 1×10^6 g/mole. Preferably, however, flocculants having a weight average molecular weight of at most 1×10^5 g/mole are used, most preferably flocculants having a molecular weight of at most 50,000 g/mole.

Long-chain polymer flocculants, such as polyacrylamides, are particularly preferred. Polyacrylamide is an acrylate polymer ($-\text{CH}_2\text{CHCONH}_2-$) formed from acrylamide sub-units that is readily cross-linked. The polyacrylamides may be modified in a conventional manner known for flocculation purposes. The weight average molecular weight of the polyacrylamide preferably ranges from 500 to

100,000 g/mole, more preferably from 600 to 50,000 g/mole, and most preferably from 700 to 5,000 g/mole.

Another particularly preferred flocculant is polyacrylic acid, a flocculant
5 employed in metal ore recovery. Polyacrylic acid is an acrylic or acrylate resin
(CH₂CHCOOH)_x formed by the polymerization of acrylic acid. It is water-soluble.
The weight average molecular weight of the polyacrylic acid preferably ranges
from 500 to 100,000 g/mole, more preferably from 720 to 50,000 g/mole.

10 In one embodiment, the polymeric catalyst according to the present invention is
a dendritic polymer. Preferably, it is a hyper-branched polymer.

Hyperbranched polymers are three-dimensional, highly branched, polymeric
molecules. The term "hyperbranched polymer" is widely used in the literature to
define a distinct class of compounds (cf. e.g. M.K. Mishra and S. Kobayashi,
15 *Star and Hyperbranched Polymers*, Marcel Dekker, 2000; US 6,399,048).
Hyperbranched polymers contain a nucleus monomer unit (also called a
"nucleus", an initiator core molecule, or a "core"), one or more generations of
branches derived from chain extender monomers, and end group functionalities
at the terminal ends of any polymeric branches. U.S. Pat. Nos. 5,859,148,
20 5,418,301, 4,507,466, 4,558,120, 4,568,737, 4,587,329, and 4,694,064, show
examples of hyperbranched polymers and methods of preparing them. Suitable
commercially available hyperbranched polymers include Boltorn[®] (from Perstorp
AB, Perstorp, Sweden). The Boltorn[®] polymers are polydispersed aliphatic
polyesters with pentaerythritol or trimethylolpropane as the core molecule. The
25 chain extender is 2,2-dimethylolpropionic acid, with the A group, and the end
group functionality, being hydroxyl. Other end group functionalities can also be
prepared by reacting the hydroxyl groups to yield epoxy or allylether
functionalities.

30 Most preferably, the polymeric catalyst according to the present invention is a
polyester amide hyper-branched polymer. A highly branched polyester amide,

hereinafter also denoted as Hybrane[®], is understood to be a linear or branched condensation polymer containing ester groups and at least an amide group in the backbone and having a number average molar mass of at least 800 g/mole. Preferably, the highly branched polyester amide has a molar mass of between
5 800 and 15,000 g/mole.

The preparation of Hybranes[®] takes place in a known manner, as for example described in WO 99/16810, WO 00/58388, WO 00/56804, and WO 02/48459. These international patent applications describe that Hybranes[®] can be prepared by reacting a cyclic anhydride or a dicarboxylic acid with an alkanol-
10 amine, preferably, a di(alkanol)amine. Another method for the preparation of Hybranes[®] is contacting a hydroxyl- or amine-functional monomer, oligomer or polymer with a first molar excess of a cyclic carboxylic anhydride, and then contacting the resulting reaction mixture with an amount of alkanol amine, the amount being a second molar excess relative to the first molar excess.

15 Suitable dicarboxylic acids for the preparation of highly branched polyester amides are dicarboxylic acids derived from C₂-C₂₄ (cyclo)alkyl, aryl or (cyclo)alkyl-aryl radicals. The dicarboxylic acids may be saturated or unsaturated. Examples of dicarboxylic acids are phthalic acid, tetrahydrophthalic acid, naphthalene dicarboxylic acid, tetrahydrophthalic acid, naphthalene
20 dicarboxylic acid, hexahydrophthalic acid, succinic acid or glutaric acid. Suitable cyclic anhydrides are phthalic anhydride, tetrahydrophthalic anhydride, maleic anhydride, (methyl)succinic anhydride, and glutaric anhydride. The alkanol- amines preferably are di(alkanol)amines, more preferably a di-β-alkanolamine. Examples are diisobutanol amine and diisopropanol amine.

25

Examples of suitable commercially available Hybranes[®] (from DSM N.V., Geleen, the Netherlands) include S1200, HA1300, and HA 1690. Hybrane[®] S1200, for example, is a dendrimeric compound based on structural units composed of succinic anhydride and di-isopropanolamine having a number
30 average molecular weight of 1,200. It has been found that this compound shows activity in inhibiting the growth of THF hydrate crystals.

Hybrane[®] HA1300 is a functionalized dendrimeric compound based on structural units composed of hexahydrophthalic anhydride and di-isopropanolamine and N,N-bis-(3-dimethylaminopropyl)amine, having a number average molecular weight of 1,300. The use of these units results in a product
5 in which the end groups are functionalized in the form of a tertiary amine group. This compound has shown a remarkable effect in inhibiting the growth of THF hydrate crystals. It has also been found that this compound can be used advantageously as a hydrate growth inhibitor in systems containing pressurized gas, condensate, and water.

10

The organic compounds suitable for halogenation using the process according to the present invention are liquid at the reaction temperature and comprise at least one aliphatic hydroxyl group, meaning that any carbon atom bearing a hydroxyl (OH) functionality does not possess more than one OH group, and that
15 it is sp³ hybridized. These OH groups can be primary, secondary, or tertiary OH functionalities. Besides the one or more aliphatic hydroxyl groups, the organic compound which is halogenated may furthermore contain heteroatoms such as a halide, sulphur, phosphorus, nitrogen, oxygen, silicon, boron, or combinations thereof. The organic compound comprising at least one aliphatic hydroxyl group
20 preferably is a C₂ – C₄₀, preferably C₃ – C₁₅, hydrocarbon, linear or branched, preferably comprising at least one primary hydroxyl group.

The organic compound to be halogenated most advantageously is a multi-hydroxylated aliphatic hydrocarbon, *i.e.* an aliphatic hydrocarbon comprising
25 two or more hydroxyl groups. Examples of such polyols are pentitols, hexitols, heptitols, octitols, decitols, dodecitol, and epoxy polyols.

More specific examples of organic compounds which are suitable for being halogenated according to the present process include ethanol, propanol,
30 butanol, pentanol, isoamyl alcohol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,3-butanediol, 1,2,4-butanetriol, 1,5-pentanediol, 1,2-

pentanediol, isopentanediol, 1,6-hexanediol, 1,2-hexanediol, 1,3-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, glycerol, ethylene glycol monoacetate, propanediol monoacetates, glycerin monoacetates, and glycerin
5 monostearates.

It is noted that the present invention can also be applied for the halogenation of carbohydrates, *i.e.* monosaccharides (e.g. glucose), oligosaccharides (e.g. sucrose), and polysaccharides (e.g. cellulose, carboxymethylcellulose). The
10 thus obtained products can be used as intermediates for the production of (fine) chemicals. This process can also be applied in a production process of ethylene dichloride (EDC) from glycol and hydrochloric acid.

In another embodiment, the process according to the present invention is used
15 for the halogenation of glycerol (1,2,3-propanetriol). In this case, preferably, glycerol is used which has been obtained as a byproduct in the production of biodiesel or during conversions of fats or oils of plant or animal origin in general, such as saponification, trans-esterification or hydrolysis reactions. Halogenated products produced from glycerol, *i.e.* dichlorohydrins or dibromohydrins, are
20 preferably used in conventional processes to produce epichlorohydrin and epibromohydrin, respectively, in the presence of a base. The preparation of epichlorohydrin can take place as described for example in *Organic Syntheses, Coll. Vol. 2*, p. 256, Vol. 16, pages 30-31 or in DE 1 075 103.

25 The hydrogen halide can be used in the form of an aqueous solution or as gaseous hydrogen halide. The use of gaseous hydrogen halide is most preferred. The hydrogen halide used in the process according to the present invention preferably is hydrogen bromide or hydrogen chloride. Hydrogen chloride is most preferred. Although the application of pure hydrochloric acid
30 (>99% pure) is preferred, a person skilled in the art will realize that the process according to the present invention is particularly suitable for application of raw

materials with only limited purity, e.g. HCl produced as a byproduct from a chemical production process.

In one embodiment of the process according to the present invention, the
5 organic compound comprising at least one aliphatic hydroxyl group is placed in a closed reaction vessel, heated, and pressurized under an atmosphere of hydrogen halide gas in the presence of the polymeric catalyst. The present invention may include various process schemes. Thus the process can be carried out in a batch reactor, preferably in fed-batch operation, or in a
10 continuously operating system such as in a cascade of continuous flow reactors of the liquid gas type.

In an exemplifying batch process, the organic compound comprising at least one aliphatic hydroxyl group which is to be halogenated and the polymeric
15 catalyst are charged to a reaction vessel. Gaseous hydrogen halide is then added to the desired pressure, and the reaction mixture is heated to the desired temperature for the desired length of time. The reaction mixture is then discharged from the reaction vessel and either purified or sent to other equipment for further processing, or to storage.

20

In an illustrative fed-batch process, one or more of the reagents are fed to a reaction vessel over a period of time throughout the reaction while other reagents are fed only at the start of the reaction. In such a process, for example, the organic compound comprising at least one hydroxyl group and the
25 polymeric catalyst may be fed in a single batch to a halogenation reactor, which is then held at reaction conditions for a suitable time, while a hydrogen halide gas is fed continuously throughout the reaction at the desired rate, which may be at constant flow, or constant pressure. After the reaction, the hydrogen halide feed can be terminated, and the reactor contents can be discharged for
30 storage, purification or further processing.

In the large-scale production of chemicals it is preferred to employ a continuous process. The continuous process may be, for example, a single-pass or a

recycle process. In a single-pass process, one or more of the reagents pass through the process equipment once, and then the resulting effluent from the reactor is sent for purification or further processing. In such a scheme, the organic compound comprising at least one aliphatic hydroxyl group and the polymeric catalyst may be fed to the equipment and hydrogen halide gas added as desired at a single point or at multiple points throughout the process equipment, which may include continuously stirred tank reactors, tubes, pipes or combinations thereof.

In a continuous recycle process, one or more of the unreacted starting material, reaction intermediates, hydrogen halide, or polymeric catalyst exiting from the process equipment are recycled back to a point earlier in the process. In this manner, raw material efficiencies are maximized and/or catalysts reused. Since catalysts are reused in such a process scheme, it may be desirable to employ the catalysts in a higher concentration than is the case in a single-pass process, where they are often discarded. This may result in faster reactions, or in smaller process equipment, which results in lower capital costs for the equipment employed.

The total mean residence time of the reaction mixture in the reactor typically is at least 1 minute, preferably at least 2 hours, and most preferably at least 4 hours. Typically, the total mean residence time is less than 24 hours, more preferably less than 18 hours, most preferably less than 12 hours.

International patent applications WO 2006/020234 and WO 2005/054167 show detailed examples of suitable equipment for carrying out the process according to the present invention.

The polymeric catalyst can be introduced into the reaction vessel neat, or as a solution in one of the reactants, e.g. glycerol, or in an appropriate organic solvent. Suitable organic solvents include alcohols and esters. The addition of the polymeric catalyst in an organic solvent is less preferred because of possible unfavourable dilution effects. The addition of the polymeric catalyst can

be performed continuously or discontinuously. The polymeric catalyst is typically used in an amount of at least 0.05% by weight, more preferably at least 0.5% by weight, and most preferably at least 1% by weight, based on the total weight of the liquid reaction mixture. Preferably, no more than 50% by weight, more
5 preferably no more than 25% by weight, and most preferably no more than 10% by weight of catalyst is employed, based on the total weight of the liquid reaction mixture.

The organic compound comprising at least one aliphatic hydroxyl group can be
10 contacted with the hydrogen halide gas in any conventional manner. For example, it can be added through nozzles, perforated plates or pipes, microporous plates, and ejectors. Typically, for each mole of hydroxyl groups to be halogenated, at least 1 mole, more preferably at least 1.1 moles, and even more preferably at least 1.2 moles of hydrogen halide gas are added. Typically,
15 no more than 200 moles, preferably no more than 100 moles, and most preferably no more than 50 moles of hydrogen halide gas are added for each mole of hydroxyl groups to be halogenated.

It may be preferred to purify the organic compound which is to be halogenated
20 before it is employed in the halogenation reaction by removing contaminants, e.g. water, organic contaminations or inorganic contaminations before use. The purification can be performed using purification techniques well known in the art, such as distillation, extraction, absorption, centrifugation, or other appropriate methods.

25

Recovery of the halogenated product can be achieved in a variety of ways. It is preferably achieved by distillation or evaporation, preferably in a continuous fashion, either directly from the reaction vessel or from a separate piece of equipment such as a vaporizer or a distillation column. Alternatively, the
30 halogenated product can be isolated via liquid extraction or absorption.

To achieve higher conversions, it might be advisable to remove at least part of the water produced during the reaction. This can for example be achieved via distillation under reduced pressure. For this purpose, use may be made of any conventionally employed device for distillation, such as evaporators of various constructions with or without a source of heat, rectification columns with various
5 internals such as trays, structured packing, random packing, etc.

The process according to the present invention is typically carried out at a temperature of at least 20°C, more preferably at least 40°C, even more preferably at least 60°C, and most preferably at least 80°C. The temperature
10 preferably is at most 160°C, more preferably at most 150°C, even more preferably at most 140°C. Most preferably, the process is carried out at the boiling point of the halogenated product to be formed.

The process is preferably carried out at a pressure of at least 0.3 bar, preferably
15 at least 0.5 bar, and most preferably it is carried out at atmospheric pressure or a pressure of at least 1 bar. Preferably, the pressure is not higher than 100 bar, more preferably not higher than 40 bar, and most preferably not higher than 20 bar.

20 With the present process, significantly lower amounts of catalyst end up in the product as compared to processes wherein prior art catalyst such as acetic acid are used, and often traces of catalyst cannot be detected at all.

The process according to the present invention is further illustrated by the
25 following examples.

EXAMPLES

Example 1

30 A mixture of 417 g (4.5 moles) of glycerol (99.5% pure, ex J.T.Baker) and 67.2 g of Hybrane[®] S1200 ex DSM in a one-litre, double-walled reactor was stirred

and heated to 95°C using an oil bath. Gaseous HCl was bubbled through the reaction mixture by means of an inlet pipe having a glass frit at its bottom to facilitate distribution of the gas into small gas bubbles. The HCl was added at a rate of 1.1 g (0.03 mole) per minute for 7 hours. In total, 474 g of HCl (13 moles) were bubbled through the reaction mixture.

The conversion was determined on the basis of the mass fractions of glycerol, monochlorohydrin (MCH), and dichlorohydrin (DCH) as measured by HPLC (with dichlorohydrin being the combined fractions of 1,3-dichloropropan-2-ol and 2,3-dichloropropan-1-ol, and with monochlorohydrin being the combined fractions of 3-monochlorohydrin and 2-monochlorohydrin). For the HPLC analysis a 300 mg sample was taken from each sample. Subsequently, 50 ml of demineralized water were added and the mixture was homogenized. This sample was analyzed using an Ion 300 Interaction column (300*7.8 mm) at 40°C using sulphuric acid 0.02 N as the eluent (injection volume of 20 µl). The flow rate was 0.4 ml per minute. An IR detector was used. Observed retention times were 23.3 min for glycerol, 29.8 min for 3-chloro-1,2-propanediol, 49.2 min for 1,3-dichloro-2-propanol, and 55.6 min for 2,3-dichloro-1-propanol.

For each mass fraction the amount of original glycerol units was determined, and the conversion was calculated as the amount of C3 units (*i.e.* a unit of three carbon atoms which is present in glycerol, MCH, and DCH) in the MCH and DCH fractions, divided by the amount of C3 units in all fractions.

The DCH selectivity was defined as $[DCH] / \{[DCH] + [MCH]\}$.

The vapour pressure of Hybrane[®] S1200 at 20°C is estimated to be less than 1 hPa.

25

The results are summarized in Table 1 and Figures 1 and 2.

Comparative Example A

A mixture of 448 g (4.86 moles) of glycerol (99.5% pure, ex J.T.Baker) and 22.6 g (0.38 mole) of glacial acetic acid (> 99.8% pure, ex Fluka) in a one-litre, double-walled reactor was stirred and heated to 95°C using an oil bath.

30

Gaseous HCl was bubbled through the reaction mixture by means of an inlet pipe having a glass frit at its bottom to facilitate distribution of the gas into small gas bubbles. The HCl was added at a rate of 1.3 g (0.04 mole) per minute for 5.5 hours. In total, 424 g of HCl (11.6 moles) were bubbled through the reaction mixture.

The vapour pressure of acetic acid is 15.8 hPa at 20.0°C and 476 hPa at 95°C. Conversions were determined as indicated in Example 1.

The results are also summarized in Table 1 and Figures 1 and 2.



In Figures 1 and 2  indicates the chlorination reaction of glycerol wherein Hybrane[®] S1200 was used as the catalyst (Example 1) and  indicates the reaction wherein acetic acid was used as the catalyst (Comparative Example A).

Table 1

Example	Catalyst	Time [h]	Glycerol conversion (%)	DCH selectivity (%)
1	Hybrane [®] S1200	0.75	29.4	5.9
	"	2.42	82.5	14.2
	"	4.34	97.3	32.2
	"	5.59	99.1	42.4
	"	6.76	99.3	51.0
A	Acetic acid	0.83	45.6	3.1
	"	2.33	91.8	20.8
	"	3.83	97.7	33.9
	"	5.5	99.2	49.2

As can be derived from Table 1, the rate of catalysis in the chlorination reaction of glycerol with HCl using a catalyst according to the present invention, Hybrane[®] S1200, is of the same order of magnitude as the rate of catalysis using the conventionally used catalyst, acetic acid. Furthermore, excellent glycerol conversion and DCH selectivity are observed.

Example 2

The following screening test was used to assess the catalytic activity. A number of small vials were filled with a mixture of glycerol and hydrochloric acid (36% aqueous solution). A typical mixture consisted of 85 wt% glycerol. To each vial
5 a different potential catalyst was added, typically about 0.2 gram to 6 grams of mixture (experiments 2(i) – 2(vii)). The vials were subsequently heated to 60-70°C and kept at that temperature for 60-80 hours. The organic composition was analyzed by HPLC. The catalytic activity was evaluated as the relative
10 amount of DCH formed in the test vial with the potential catalyst of concern compared to the DCH formed in the blank test-vial, i.e. without addition of a catalyst (comparative experiment B). The results are summarized in Table 2. As can be derived from Table 2, good to reasonable catalyst activities were observed, as well as good DCH selectivities.

15

Hybrane[®] S1200 and Hybrane[®] HA1690 were obtained from DSM, Geleen, The Netherlands. The polyacrylic acids (with a Mw of 2,000, 100,000, 1,250,000, and 100,000) were obtained from Aldrich, Zwijndrecht, The Netherlands. The polyacrylic acid with a Mw of 100,000 was a 35% solution in water and was
20 used as such. Polyacrylamide was obtained from Aldrich, Zwijndrecht, The Netherlands, and had a Mw of 1,500.

Table 2

Entry	Catalyst	Mass	Relative mol fraction [mol%]			
		fraction catalyst [wt%]	glycerol	1-MCH	1,3-DCH	Total
B	none		95.3%	4.7%	0.0%	100.0%
2 (i)	polyacrylamide	8.8%	35.2%	56.7%	8.2%	100.0%
2 (ii)	Hybrane [®] S1200	3.0%	0.6%	60.7%	38.7%	100.0%
2 (iii)	Hybrane [®] HA1690	2.1%	0.3%	81.1%	18.6%	100.0%
2 (iv)	polyacrylic acid, MW=2,000	5.0%	14.5%	61.5%	23.9%	100.0%
2 (v)	polyacrylic acid, MW=100,000	13.7%	36.2%	52.8%	11.0%	100.0%
2 (vi)	polyacrylic acid, MW=1,250,000	4.8%	67.6%	27.2%	5.2%	100.0%
2 (vii)	polyacrylic acid, MW=4,000,000	4.9%	69.7%	25.4%	4.9%	100.0%

CLAIMS

1. Process for the catalytic halogenation of an organic compound comprising at least one aliphatic hydroxyl group which comprises the step of
5 contacting the organic compound comprising at least one aliphatic hydroxyl group with a hydrogen halide in the presence of a catalyst, with said catalyst being an organic polymer which comprises at least one carbonyl group, has a vapour pressure at the reaction temperature of less than 1 mbar, has a weight average molecular weight M_w of 500 g/mole or
10 more, and is soluble in the reaction mixture at the reaction temperature.
2. A process according to claim 1 wherein the catalyst is a dendritic polymer or an organic flocculant.
- 15 3. A process according to claim 2 wherein the catalyst is a polyester amide hyper-branched polymer, polyacrylamide, or polyacrylic acid.
4. A process according to any one of the preceding claims wherein the
20 organic compound comprising at least one aliphatic hydroxyl group is a C_2 - C_{40} , preferably C_3 - C_{15} , hydrocarbon, linear or branched, comprising at least one hydroxyl group.
5. A process according to claim 4 wherein the organic compound comprising
25 at least one hydroxyl group is selected from the group consisting of ethanol, propanol, butanol, pentanol, isoamyl alcohol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,3-butanediol, 1,2,4-butanetriol, 1,5-pentanediol, 1,2-pentanediol, isopentanediol, 1,6-hexanediol, 1,2-hexanediol, 1,3-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol,
30 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, glycerol, ethylene glycol monoacetate, propanediol monoacetates, glycerin monoacetates, glycerin monostearates, and glycerin diacetates.

6. A process according to any one of the preceding claims wherein the hydrogen halide is gaseous hydrogen chloride.
- 5 7. A process according to any one of the preceding claims wherein for each mole of hydroxyl groups to be halogenated, between 1 and 200 moles of hydrogen halide gas are added.
8. A process according to any one of the preceding claims wherein the
10 process is carried out at a temperature of between 20° and 160°C.
9. A process according to any one of the preceding claims wherein the
organic compound comprising at least one aliphatic hydroxyl group is
glycerol and the hydrogen halide gas is hydrogen chloride or hydrogen
15 bromide.
10. A process according to claim 9 wherein the resulting halogenated products
are used to prepare epichlorohydrin and epibromohydrin, respectively, by
contacting them with a base.

Figure 1

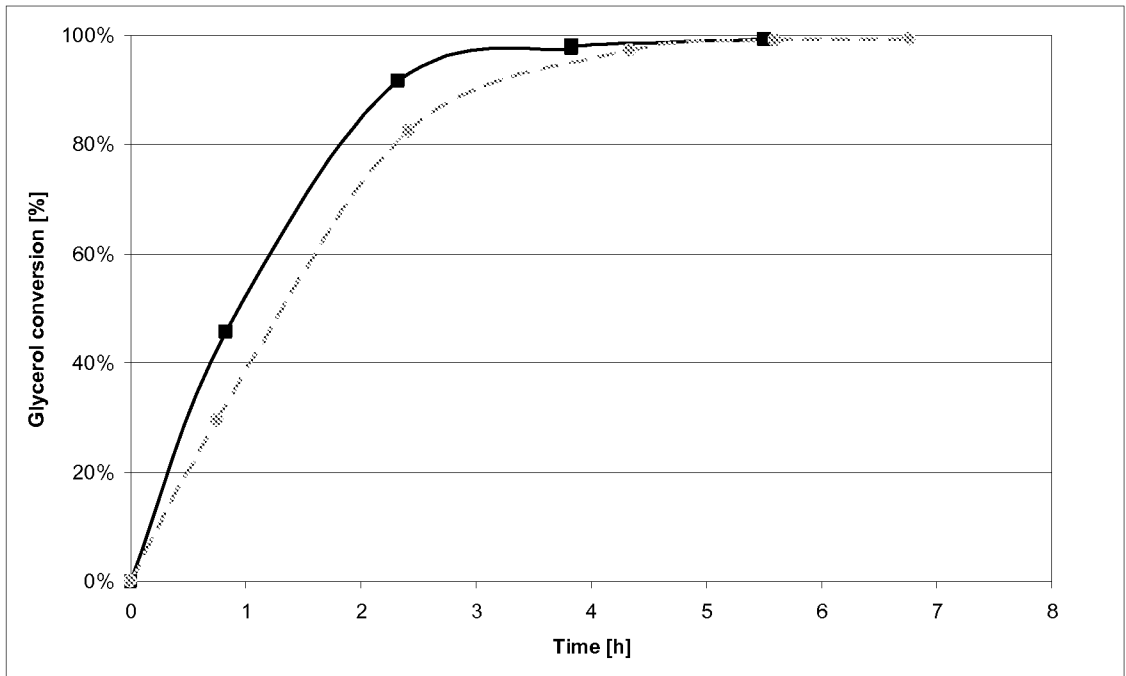
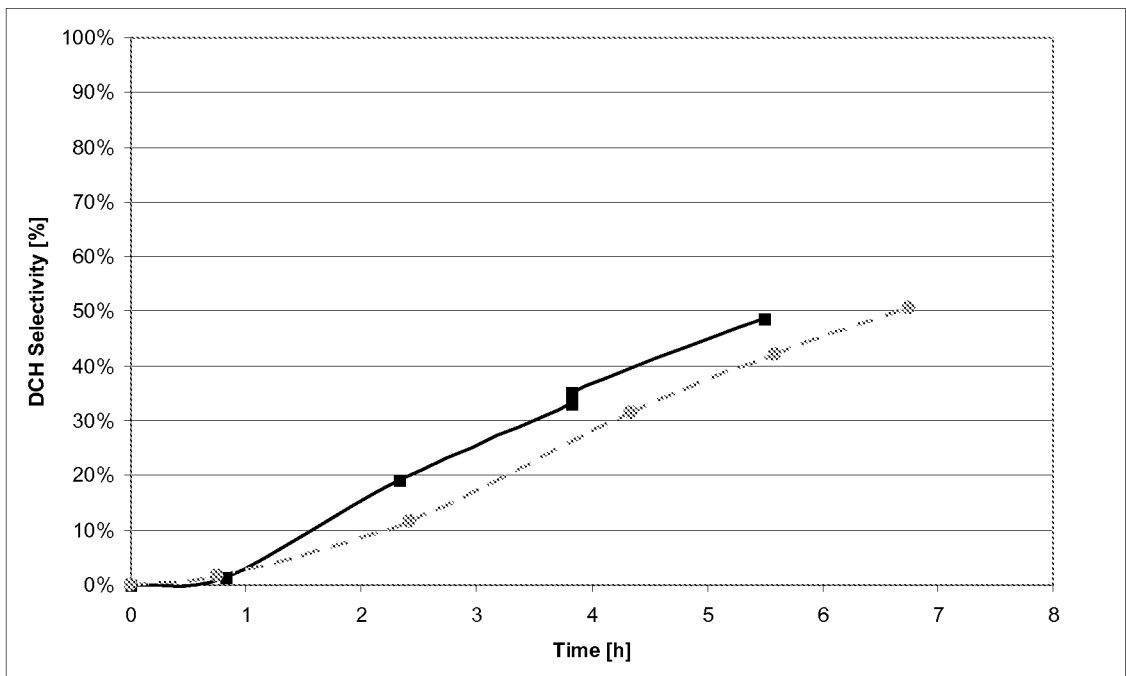


Figure 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/063944

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C29/62 C07D301/26 C07D303/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, BEILSTEIN Data, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2006/020234 A (DOW GLOBAL TECHNOLOGIES) 23 February 2006 (2006-02-23) cited in the application claim 1; examples 37,38	1-10
A	A. BOUILLAUD, ET AL.: "Synthesis of dibromohydrins from glycerol by using an ion exchange resin as catalyst" AUSTRALIAN JOURNAL OF CHEMISTRY, vol. 47, no. 11, November 1994 (1994-11), pages 2123-2128, XP009087148 COLLINGWOOD, VICTORIA, AU ISSN: 0004-9425 the whole document	1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/063944

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006020234 A	23-02-2006	EP 1771403 A1	11-04-2007
		JP 2008507526 T	13-03-2008
		US 2008045728 A1	21-02-2008
