

Propylene Glycol Monomethyl Ether Propionate and
a Process for the Preparation thereof

This invention relates to propylene glycol monomethyl ether propionate, particularly as obtained by the reaction between propylene glycol monomethyl ether and propionic acid, as well as a process for the preparation of the same.

Organic ester compounds are good solvents widely used in synthetic resin industry, such as for paints, inks, adhesives and detergents. At present, ether compounds are mainly divided into two categories, i.e. E series and P series. The E series of ether compounds are obtained from the reaction of alcohols and ethylene oxide while P series of ether compounds are obtained from the reaction of alcohols and propylene oxide. The related ester compounds thereof are primarily acetate esters, whereas no propionate ester products have been developed so far.

In recent years, it has been found that the E series of ethers or acetate ester compounds thereof, when inhaled into the human body, are probably decomposed into alkoxy acetic acid ethers which induce erythrocytes to become abnormal and thus toxic to the genital organ. On the other hand, P series would not cause these damages.

At present, propylene glycol monomethyl ether acetate of P series is inferior in its solubilisation of unsaturated polyesters or polyurethane resins as well as the drying capability of the coating thereof. Therefore, it is urgently demanded to develop a kind of solvent having not only excellent solubilisation and drying capability but also low toxicity.

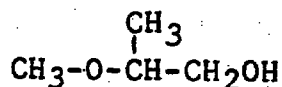
Consequently, the inventors of the present application have endeavored in positive research and development, and eventually produced successfully propylene glycol monomethyl ether propionate.

An object of the present application is to provide the novel compound propylene glycol monomethyl ether propionate.

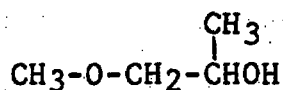
Another object is to provide a process for the preparation of propylene glycol monomethyl ether propionate (called "PMP" hereafter), which comprises reacting propylene glycol monomethyl ether (called "PGM" hereafter), obtained by reaction of methanol and propylene oxide under high pressure at high temperature, and propionic acid in the presence of acidic catalyst.

A further object is to use PMP as a solvent, especially in the fields of paints, inks, adhesives and detergents industries.

The starting material PGM used for the present invention is usually presented as an isomeric mixture consisting of primary PGM having the formula of

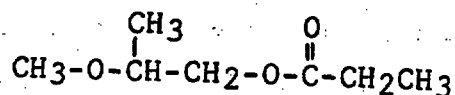


and secondary PGM having the formula of

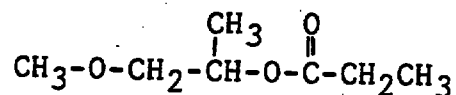


If PGM is produced by reaction of propylene oxide in the presence of an acidic catalyst, the ratio between primary and secondary PGMS presented in the mixture will be about 55:45, whereas in the presence of an alkaline catalyst, the ratio will be 2:98.

In carrying out the reaction with propionic acid, when primary PGM is used a primary PMP of the formula



is obtained, and when secondary PGM is used a secondary PMP of the formula



is obtained correspondingly. In alternative nomenclature the primary PMP is 2-methoxy-1-propyl propionate while the secondary PMP is 1-methoxy-2-propyl propionate.

Since primary PGM is harmful to the human body, the secondary PGM is preferred in the invention according to the present application. Consequently, PGM produced in the presence of an alkaline catalyst is used in the present invention as it is substantially free of primary PGM and, hence, produces substantially pure secondary PMP.

As referred hereinafter in the specification and claims, both PGM and PMP mean the mixture of predominantly the secondary and minor or trace amounts, namely below 2% by weight, of the primary isomers.

The process for the preparation of PMP according to the present invention can be either a batch or a continuous process. In general when the moisture generated during the reaction is not removed, the reaction system reaches an equilibrium state which hinders the increase of yield and thus is disadvantageous to

industrial production. Therefore, in the process of the present invention, no matter whether a batch or continuous process is adopted, an azeotropic agent should be added to the reaction system. Many aromatic solvents are suitable as azeotropic agents.

In the batch process, the reactants and azeotropic solvent are placed into the reactor for carrying out the reaction and heated at the azeotropic temperature while removing the water and recycling the azeotropic solvent. After the end of the reaction, the product and azeotropic solvent are separated by fractional distillation so as to obtain a product of high purity.

In the continuous process, the starting materials are fed into the reactor at a given flow rate and the water is withdrawn continuously from the top of the fractionator during the progress of the reaction. The azeotropic solvent is recycled while the reaction system containing the product PMP, when it has reached a certain concentration, is transferred into a distillation tower, fractional distillation of the mixture removing minor amounts of unreacted ether, acid and PMP. Thereby, a product of high purity is obtained.

According to the process for the preparation of PMP in the present application, the starting materials of PGM and propionic acid are reacted at an elevated temperature

above 80 °C in the presence of acidic catalyst and azeotropic agent so as to produce crude PMP. The product is then separated by distillation so as to remove the unreacted acid and generated water, to obtain PMP of high purity.

For the starting materials, the molar ratio of PGM to propionic acid is generally in the range of 0.6 to 3.0, preferably from 1.0 to 2.0, in which PGM is in excess with respect to propionic acid. If the molar ratio is smaller than 0.6 or greater than 3.0, after the reaction is accomplished, unreacted starting materials are present in great excess so that not only more energy consumption is rendered during the distillation process, but also the distillation time required is increased so as to decrease the rate of production of pure PMP. If propionic acid is added in excess, namely the molar ratio of PGM to propionic acid is smaller than 0.6, the reaction rate drops remarkably. The reason is unclear but it is assumed that the acidic catalyst is subjected to buffering.

The catalysts used in the present invention include inorganic acids, such as sulfuric acid, hydrochloric acid and phosphoric acid, and organic acids, such as acetic acid, oxalic acid, citric acid, p-toluene sulfonic acid and methane sulfonic acid, among which the strong acids including sulfuric acid, p-toluene sulfonic acid or methane sulfonic acid are preferred. Propylene glycol

monomethyl ether propionate obtained according to the present application has a boiling point of 160.5 °C, while other reactants and products having respective boiling point of 120 °C for PGM, 140.8 °C for propionic acid and 100 °C for water. It is easier to fractionally distill this mixture compared to the conventional mixture having the respective boiling point of 146 °C for propylene glycol monomethyl ether acetate, 118 °C for acetic acid and 120 °C for PGM as in the conventional case. This is one of the effects achieved by the process according to the present invention.

Another effect achieved is lower toxicity of PMP against the metabolic organs. In accordance with NOEL (NO Observable Effect Level) published by Environment Protection Agency of U.S.A., E and P series of esters for rabbit are 30 and 3000 ppm, respectively. PMP of this invention belongs to P series and thus has very low toxicity against the genital organ.

Further, PMP has better solubility for various resins. For example, propylene glycol monomethyl ether acetate has final solvent percentage of 70% to alkyd resin, while PMP is over 90%, such that an excellent solvent is herewith proved.

In the process of the present invention, when the reaction is completed the reaction system must be treated

by double distillation. Primary distillation is a dehydration and deacidification procedure. For enhancing the efficiency and saving energy, an azeotropic agent selected from aromatic organic solvents such as benzene, toluene, xylene and cyclohexane is added in amount of 6 to 30%, by volume preferably from 8 to 15% by volume, with respect to combined starting materials in order to reduce the azeotropic temperature in distillation. If the amount of azeotropic agent added is lower than 6% the residue of unreacted acid cannot be completely removed. On the contrary, if the amount is higher than 30% then the solvent will occupy a relatively greater capacity, which will consume a great quantity of energy and hence be economically unfavourable. During secondary distillation, only two components of ether and ester are left, which are almost completely separable by fractional distillation, based on the difference of boiling points between the two components, such that a product of high purity is obtained.

Now, the present invention will be further described by means of the following Examples which are merely for the purpose of illustration and are by no means limiting in their scope, with reference to the accompanying Figures in which:

Figure 1 is a ^1H nmr spectrum of PMP produced according to the present invention; and

Figure 2 is a mass spectrum of PMP produced according to the present invention.

Example 1

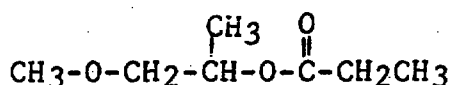
Into the reactor having a volume of 3 liters, 1172 ml of PGM and 746 ml of propionic acid were introduced. After mixing 200 ml of xylene and 10 grams of p-toluene sulfonic acid were added. Then the mixture was brought to reflux temperature at 142 °C and the reaction carried out for 5 hours at this temperature. During this period water was removed simultaneously so as to favour of the progression of the reaction. The reaction solution was analyzed by gas chromatography and the following composition found:

PMP	69.91 %
PGM	15.34 %
propionic acid	6.33 %
xylene	7.78 %
water	0.59 %

This solution was further treated by double distillation, PMP compound having a purity greater than 99.5% being obtained.

This PMP compound was characterized by the ^1H nmr spectrum as shown in Fig. 1 and mass spectrum as shown in Fig. 2. Thereby the chemical structure thereof can be

determined as having the formula



In other words, substantial pure secondary PMP is obtained and primary PMP is present in an almost undetectable amount.

Example 2

Into the reactor having a volume of 3 liters, 1172 ml of PGM and 746 ml of propionic acid were introduced. After mixing 10 grams of P-toluene sulfonic acid were added. Then the temperature was brought to 99.1 °C, the azeotropic temperature of water and propionic acid, and the reflux reaction carried out for 5 hours. Since no azeotropic solvent was added, the aqueous layer was impossible to separate, such that equilibrium was probably reached. This reaction solution was analyzed by gas chromatography and found the following composition.

PMP	44.6 %
PGM	27.6 %
propionic acid	22.4 %
water	5.4 %

Comparative Example

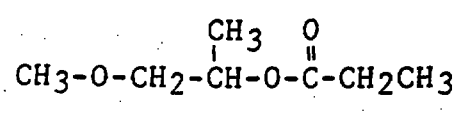
Into the reactor having a volume of 3 liters, 1172 ml of PGM and 572 ml of acetic acid were introduced. After mixing, 10 grams of p-toluene sulfonic acid were added. Then the temperature was brought to the reflux temperature of 97.5 °C to carry out the reaction for 5 hours. The reaction solution was analyzed by gas chromatography and found the following composition:

propylene glycol monomethyl ether acetate	44.0	%
acetic acid	20.1	%
PGM	29.7	%
water	5.8	%

This solution was treated by double distillation and propylene glycol monomethyl ether acetate having a purity of 99% was obtained. The yield is too low to meet the industrial requirement.

Claims

1. Propylene glycol monomethyl ether propionate.
2. Propylene glycol monomethyl ether propionate compound according to Claim 1, having predominantly the formula



3. A process for the preparation of propylene glycol monomethyl ether propionate, comprising the steps of reacting propylene glycol monomethyl ether and propionic acid at elevated temperature above 80 °C in the presence of acidic catalyst and azeotropic agent to promote esterification, to produce crude propylene glycol monomethyl ether propionate and removing the unreacted acid and water by distillation to obtain propylene glycol monomethyl ether propionate having high purity.
4. A process according to Claim 3 wherein the propylene glycol monomethyl ether used is predominantly 1-methoxy-2-propanol.



5. A process according to Claim 3 or Claim 4, wherein the molar ratio between propylene glycol monomethyl ether and propionic acid is in the range from 0.6 to 3.0.
6. A process according to any of Claims 3 to 5, wherein said catalyst is selected from a group consisting of sulfuric acid, p-toluene sulfonic acid and methane sulfonic acid.
7. A process according to any of Claims 3 to 6, wherein said azeotropic agent is selected from a group consisting of benzene, toluene, xylene and cyclohexane, in an amount of 6% to 30% by volume with respect to the sum of propylene glycol monomethyl ether and propionic acid.
8. Use of propylene glycol monomethyl ether propionate as a solvent.
9. Use according to Claim 8, as a solvent for paints, inks, adhesives or detergents.

