

# pH DISTRIBUTION CONTROL IN INDIRECT ANODIC PROPYLENE OXIDATION

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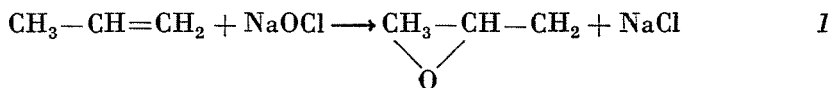
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Manufacture of propylene oxide is of primary concern in our days since it is an important and indispensable prime material for a number of organic products, chiefly plastics. As it is widely known, propylene oxide can be produced both in traditional, usual chemical way and by electrochemical oxidation of propylene. At any rate, electrochemical methods seem to be preferred to the pure chemical ones — especially during the last decade — thanks to their advantages of simplicity, selectivity and rather expedient control of the critical process variables. This control can usually be carried out by adjusting parameters basic to electrolysis *e.g.* voltage, electrode potential, overvoltage (choosing appropriate electrode materials) as well as current density, as usual.

In practice, however, difficulties emerge in connection with the actual conditions of the electrochemical process. These difficulties are — theoretically speaking — due to the reaction mechanism of the propylene oxidation characterized by the over-all reaction 1:

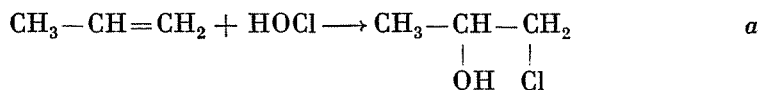


In this process the sodium hypochlorite is seen to enter into chemical reaction with the propylene molecules. As oxidants — or, more exactly speaking, oxygen carriers — hypochlorite or hypobromite anions come into account in the overwhelming majority of cases of practical importance, quite apart from the question of whether direct or indirect anodic oxidation has been resorted to.

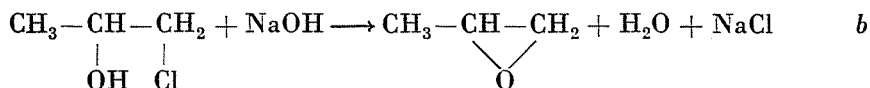
## Fundamentals

Said reaction mechanism consists of two essential consecutive steps (ignoring side reactions). In the first step the hypochlorite reacts with the

dissolved propylene resulting in chlorohydrin as written in the reaction *a*:



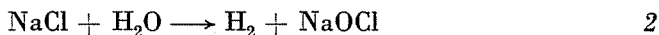
whilst in the second step the chlorohydrin intermediates are converted into propylene oxide having been contacted with some basic compound *e.g.* sodium hydroxide irrespective of its origin, see reaction *b*:



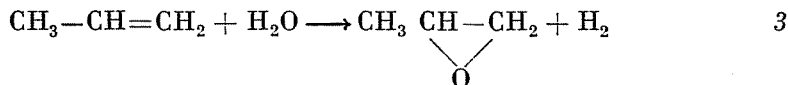
Sodium chloride re-enters thereafter the electrochemical unit of the cycle to be repeatedly transformed into sodium hypochlorite.

It is obvious that the net process of the reactions *a* and *b* is in any case the reaction *1* *i.e.* the production of propylene oxide from propylene and sodium hypochlorite.

Reaction sequence, however, cannot be treated independent of the electrolysis that hypochlorite anions will be produced in. Electrochemical step, as a matter of fact, is also carried out in the technological closed cycle itself (*cf.* reaction 2) and the sodium chloride takes part likewise in the cycle. Mechanism of electrochemical hypochlorite production — being widely known — needs no interpretation:



Hence, production of propylene oxide from propylene and water is to be taken for the real net process after all:



It is open-and-shut that the sum of reactions *1* and *2* is the net process *3* treated.

Difficulties of principle mentioned are inherent in the totally different conditions of the two steps treated. Reaction *a* is seen to be connected with proton addition *i.e.* consuming hydronium ions whilst in reaction *b* (second step) hydroxyl anions are needed for removing protons from the chlorohydrin intermediate. From another aspect — from practical point of view — the first step of the propylene oxide production treated requires decrease in pH (in other words: acidification), the second, however, in contrast to the first

one, increases in pH (alkalification). Besides, reaction *a* is, as a matter of fact a redox process at the same time and to shift the equilibrium towards formation of the product (in our case: of the intermediate) acidification is necessary even in this respect. Nevertheless increase in acid and hypo concentration isn't advantageous on account of the acceleration of undesired side reactions such as decomposition of hypochlorite into elemental chlorine and sodium chloride, disproportionation of hypochlorite into chloride and chlorate anions as well as formation of dichloro-propane. Accordingly, a rather narrow pH interval is to be maintained for the sake of the selectivity of the process. Strict pH demands set limits to the rate of the reaction *I* as well as to the productivity of processes based on it, because pH conditions fail to provide productivity acceptable in practice whensoever propylene and sodium hypochlorite are contacted directly.

Taking the governing role of the pH distribution in the process treated into consideration, alternating anodic and cathodic treatment of propylene dissolved in sodium chloride solution has been suggested in the majority of relevant publications in order to utilize the effect of anodic acidification and cathodic alkalification, respectively, in the vicinity of corresponding electrodes in diaphragm cells. These known local pH deviations are due to the mechanism of electrode processes during the electrochemical decomposition of water. The halohydrin-forming reaction (cf. reaction *a*) may be carried out by contacting the olefin with anolyte within the cell or in a contacting tower external of the cell proper or partially in both. The halohydrin containing aqueous medium is then subjected to dehydrohalogenation in order to convert the halohydrin to olefin oxide by treatment with the alkaline catholyte. The dehydrohalogenation step may be carried out in the alkaline catholyte contained within the cell itself or in a step outside of the cell or partially in both. These various methods are described in further detail in U.S. Patent No. 3 288 692 and Belgian Patents No. 705 083 and No. 705 084.

Unique feature of the method is a particulate phase between the electrodes consisting of a packed bed of electronically conducting beads as treated in papers by Goodridge, Fleischmann and others (25th Meeting of I.S.E. Brighton, 1974, Extended Abstracts pp. 11—13). Under suitably chosen conditions — if the specific resistance of the solution is great enough — these conducting beads act as bipolar electrodes contributing to the intensification of the process.

### Practical

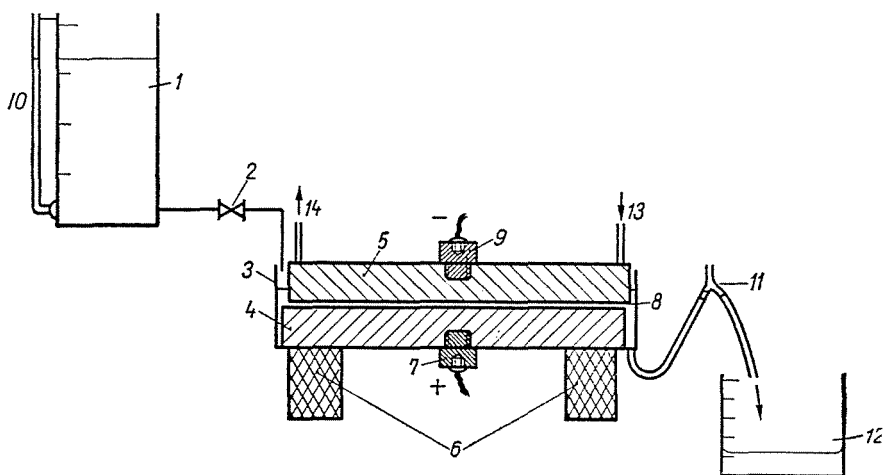
Attempts made to solve the problem show — even without entering into further details — that direct connection of the electrochemical hypo production and propylene chemisorption leads to a number of constructional diffi-

culties as well as to cumbersome operation each time the local pH differences in the electrolyte are expected to provide a reaction rate needed in practice. Hence, an other effect for maintaining the necessary pH distribution seemed desirable with special regard to the utilization of industrial hypo cells already proved practicable in other fields.

Present work is concerned with propylene oxidation according to the reaction 1 when both proton addition and removal in reaction steps *a* and *b* are based on the considerable temperature dependence of carbon dioxide solubility in aqueous media.

pH regulation in chemical rather than electrochemical way in the process in question enables continuous hypochlorite production outside the propylene chemisorption zone. Consequently, electrolyser for producing hypochlorite anions can be designed even in the most simple way like exemplified in Fig. 1 according to which hypochlorite will be produced between two parallel graphite planes without diaphragm therebetween. Scale-up of this electrolyser is likewise very simple by multiplying said graphite plane units as shown in Fig. 2. However, application of any other commercial electrolyser for hypo production can also be reckoned with, quite apart from its original destination *e.g.* laundry service.

Considerable advantage of propylene oxidation by means of hypochlorite cells independent of the propylene chemisorption lies in the simplicity of the electrolysis on the one hand and in optional adjusting of the optimum electrolysis parameters on the other. Latter standpoint is especially worthy of attention considering energy conditions of electrochemical sodium hypochlorite



**Fig. 1.** Graphite electrode hypo cell. 1 Sodium chloride feed-tank; 2 admission valve; 3 electrolysis vat; 4 anode block; 5 cathode block; 6 cell pads; 7 anode connection; 8 electrode gap; 9 cathode connection; 10 calibrated leveller tube; 11 outlet pipe; 12 hypo tank

manufacture according to diagram 3. Curve *A* represents here the specific energy requirement of the electrolysis in kWh/kg active chlorine, *Y* the current efficiency, whilst *G* the conversion in kg sodium chloride/kg active chlorine as function of active chlorine concentration in the produced solution  $Cl^a$  in g/l. Since the process necessitates a quite dilute hypochlorite solution, energy conditions are decidedly fortunate: energy requirement doesn't exceed 3.2 to 3.4 kWh/kg  $Cl^a$  due to the high current efficiency at about 3 to 4 g  $Cl^a$ /litre electrolyte. On the other hand, since sodium chloride solution takes part in a continuous recirculation between the chemisorption column and the electrolyser, the relatively high figures of the conversion *G* cannot be taken for a practical drawback either.

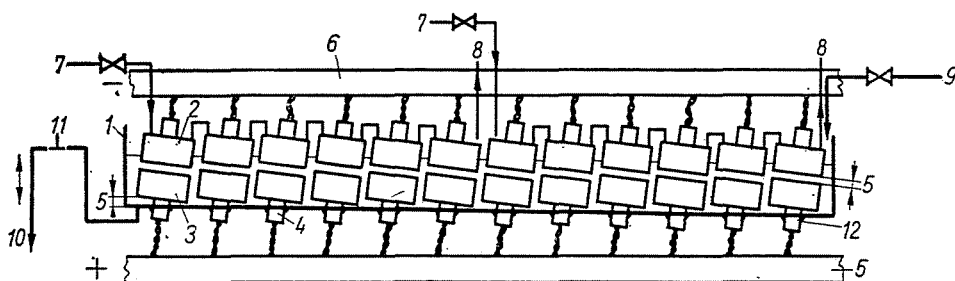


Fig. 2. Industrial scale hypo cell. 1 Electrolysis vat; 2 cathode blocks; 3 anode blocks; 4 anode connection; 5 anode bus-bar; 6 cathode bus-bar; 7 cooling water inlet; 8 cooling water outlet; 9 sodium chloride input; 10 hypo output; 11 outlet pipe; 12 gasket seats

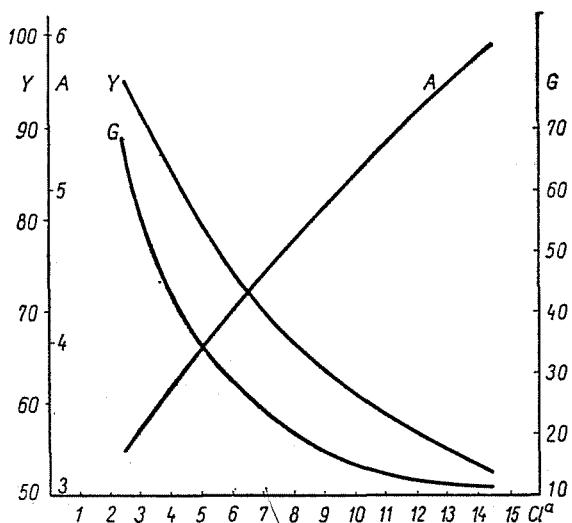


Fig. 3

The practical carrying out of pH control according to this method is surprisingly simple as shown in Fig. 4. The sodium chloride solution containing about 2 or 3 grams of active chlorine per litre is fed from the electrolyser 1 into the cooler 2 continuously, then the solution enters the chemisorption tower, *i.e.* chlorohydrin reactor 3 about one meter high and 50 mm in diameter, filled with indifferent Raschig rings. Propylene and carbon dioxide are fed into the same tower from below in countercurrent and the velocity of solution and of the two gases are adjusted according to the sense calculated stoichiometrically so that the stationary pH in the bulk of the chemisorption zone is about 4.5 to 5.0. An additional advantage of the proton "feeding in" by carbon dioxide in the treated way lies in the elimination of undesired side reactions detailed above since pH has been stabilized in the favourable region like this. Hence, it is the reaction *a* that takes place almost exclusively in the tower.

The chlorohydrin containing solution enters thereafter the evaporator 4 that the dehydrohalogenation (reaction *b*) is carried out in owing to the carbon dioxide split at about 45 °C. Equilibrium of the reaction is strongly shifted towards formation of the propylene oxide thanks to its continuous removal from the evaporator after being distilled out of it.

All the gases from the tower 3 and evaporator 4 enter thereafter the condenser 5 where the propylene oxide will be condensed then separated from the gases in the separator 6, whilst sodium chloride solution practically devoid of propylene oxide is recycled from the evaporator 4 into the electrolyser 1 by means the pump 7.

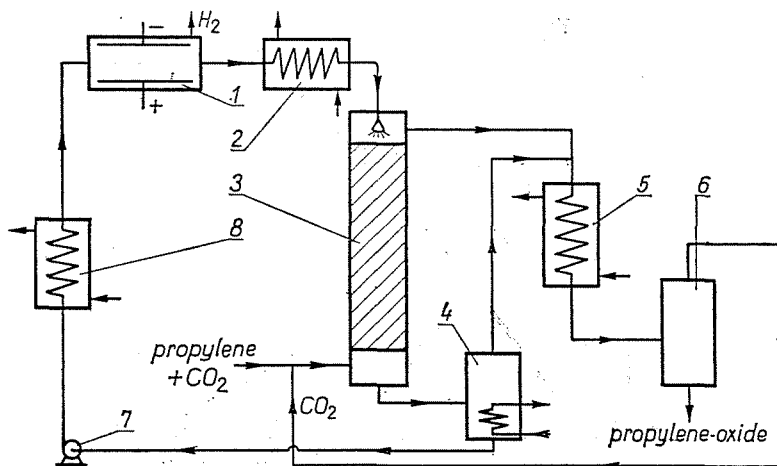
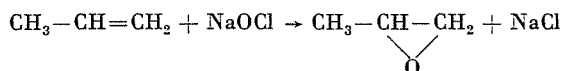


Fig. 4

Obviously the scale-up of electrolyser, of chemisorption tower and other accessories of the apparatus needs no special improvement in equipment and fittings, hence the method is expected to become soon of practical importance.

### Summary

Propylene oxidation according to the reaction



has already been investigated far and wide. For the sake of maintaining continuity of the "closed cycle" anodic chloride oxidation — chemical propylene oxidation special care should be placed upon pH control. Instead of diaphragm cell anolyte — catholyte mixing (generally believed as promising) a stationary pH distribution is maintained in the chemical reaction unit itself by means of alternating carbon dioxide absorption — desorption that aims at a considerable simplification in comparison to methods published so far.

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