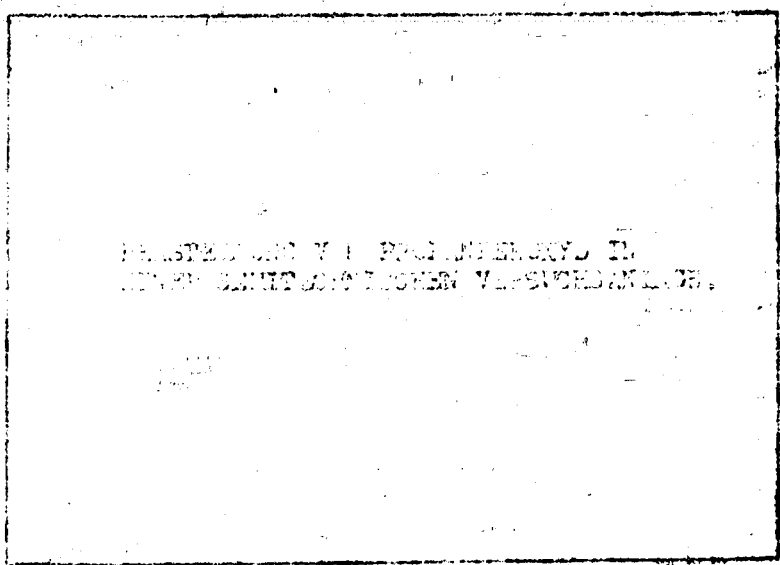


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**PRODUCTION OF PROPANE PEROXIDE IN A
SEMITECHNICAL EXPERIMENTAL PLANT**

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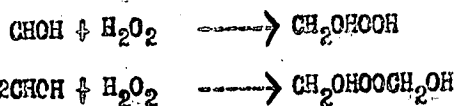
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Frames 2424-2430

Translation

INTRODUCTION

By oxidation of propane with oxygen under proper conditions one obtains liquid reaction products, which are subsequently designated with the name "propane peroxide", and which consist chiefly of a mixture of water, hydrogen peroxide and oxyalkyl peroxides. These oxyalkyl peroxides are formed after the condensation of reaction products from the reaction of the aldehydes formed (chiefly formaldehyde) and hydrogen peroxide, according to the equations:



Consequently, the amount of free hydrogen peroxide in the reaction product is dependent on the ratio between the amount of aldehyde and the amount of hydrogen peroxide.

Under the best reaction condition (temperature of 465 C, contact time - 5 seconds), the free hydrogen content in the solution amounts to about 60 per cent by molecular weight, corresponding to the total amount in the peroxide.

The following patent claims are made for the actual process as used industrially.

I. Dutch Patent No. 52521.

Process for the preparation of peroxide by incomplete burning of hydrocarbons (presented on April 10, 1940, granted on December 15, 1941).

Patent Claim:

1. Process for the preparation of peroxide by the incomplete burning of hydrocarbons, characterized by the fact, that the wall of the space, in which the burning takes place, consists of non-rusting metal and that the wall temperature does not exceed 200 C.
2. Process according to 1., characterized by the fact, that a reaction vessel of great volume in proportion to its surface is employed, for example, a spherical reaction vessel.
3. Process according to 1., characterized by the fact, that the gas flows along on the wall of the reaction vessel, whereupon

one can react it within the reaction vessel.

4. Process according to 1., characterized by the fact, that the reaction product is drawn off and cooled quickly. 2428

II. Dutch Patent No. 52522.

Process for the production of hydrogen peroxide by incomplete burning of gaseous saturated hydrocarbons with two or more carbon atoms (presented on April 10, 1940, granted December 15, 1941).

Patent Claims:

1. Process for the preparation of hydrogen peroxide, characterized by the fact, that gaseous saturated hydrocarbons with two or more carbon atoms in a molecule are incompletely burned in the case of a temperature between 440 and 500 C with the aid of oxygen, whereby the volume ratio between these hydrocarbons and oxygen amounts to at least 4:1, preferably 7:1 or more.

2. Process according to 1., characterized by the fact, that the reaction products formed, dependent on the pressure, are cooled so far, that the desired hydrogen peroxide goes over into the liquid reaction product and secondary products, as formaldehyde and acetaldehyde, remain in the vapor state.

III. Dutch Patent No. 55114.

Process for the production of hydrogen peroxide out of incomplete combustion products of gaseous hydrocarbons by fractional distillation after the removal or transformation of organic peroxides present (presented on August 5, 1941, granted on March 15, 1943).

Patent Claims:

1. Process for the preparation of hydrogen peroxide out of incomplete combustion products of gaseous hydrocarbons, characterized by the fact, that the hydrogen peroxide is obtained by fractional distillation, after the organic peroxides present are removed or transformed.

2. Process according to 1., characterized by the fact, that the organic peroxides are removed by transformation into acids, whereat the incomplete combustion products are heated a short time, preferably at a temperature between 40 and 100 C.

3. Process according to 1. or 2., characterized by the fact, that the fractional distillation is so undertaken that a mixture of water and acids pass out of the top of the first rectifying column and hydrogen peroxide base products remain; the above mixture, which passes out of the column, is brought into a second rectifying column, about in the middle and the water vapor coming out of this column is sent back over a condenser into the distillation reservoir. 2427

**PROCESS AND DESCRIPTION OF THE
SCHEME OF THE SEMITECHNICAL APPARATUS**

A mixture of $12.7\text{m}^3/\text{hr}$ of highest possible percentage propane (1) and $4.8\text{m}^3/\text{hr}$ oxygen (5) are fed to the reaction chamber (2) by means of a reducing valve and flow meter. In place of the oxygen nitrogen (4) can be fed to the apparatus in an emergency. Since a great area of the decomposition accelerates the peroxides formed in the case of the reaction, the reaction vessel--in order to hold the surface-volume ratio as small as possible--is built in a spherical shape.

In order to avoid a decomposition of the propane peroxides formed, the reaction vessel (described in Patent No. 52521) is covered inside with V_2A steel and supplied with an air-cooling jacket, which permits cooling of reaction surface to a temperature, which lies above the dew point of the reaction's efficiency.

The propane/oxygen mixture is fed to the sphere through a ring-shaped slot, so designed that it flows along the surface and results in a rotary motion.

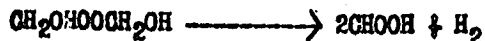
For the introduction of the reaction, the mixture is ignited with a spark plug. After the reaction has begun, ignition is no longer necessary. The reaction temperature is regulated at about 465 C by variation of the oxygen content of the gases supplied. Probably the desired percentage of oxygen is lower than stated in the scheme.

The gaseous reaction mixture is transferred by the piping (6), which is cooled only to a point, where water formed in the reaction chamber lies above its dew point, to the cooler (7) and there cooled to about 35 C . At this temperature there remains still considerable amounts of aldehyde (acetaldehyde) in the gaseous state, whereby the free hydrogen peroxide content of the reaction liquid is greater than if one cooled to a lower temperature.

The liquid mixture which leaves the cooler passes a second ice cooler (8), where it is cooled to 0 C , in order to stop undesirable decomposition, and is collected in the accumulator (9). Per hour about 1.5 liters of liquid peroxide is formed with an active oxygen content of about 18 mg equivalent per cm^3 . Of this 18 mg equivalent, almost 10 mg equivalent are hydrogen peroxide and 8 mg equivalent oxyalkyl peroxide.

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In order to separate the hydrogen peroxide from solution in a rectifying column not indicated in the scheme, the organic peroxides are changed selectively into formic acid (acetic acid) and hydrogen according to the equation:



while the hydrogen peroxide is practically not affected.

By rectification with vapor there is obtained 50 per cent

hydrogen peroxide and formic acid (acetic acid)

The reaction gas ($16.3m^3/hr$) left behind in the cooler (7) and not condensed is compiled as follows:

0.6 %	CO_2
8.8 %	O_2H_6
3.2 %	O_2
3.0 %	CO
0.1 %	H_2
84.3 %	C_3H_8

This gas is extracted from propane by means of a sulfuric acid bath (11) part of which is circulated back to the reaction chamber (2) by means of a recycle pump (10).

PRODUCTION WITHOUT CIRCULATION

According to the share out of $12.7m^3/hr$ of propane 1.5 liters/hr of propane peroxide is obtained; out of $100m^3/hr$ of propane, 12 liters/hr of propane peroxide is thereby obtained (specific weight = 1.1).

With a yield of 10 mg equivalent of H_2O_2 per cm^3 and a rectification yield of about 70 per cent, there can therefore be obtained per $100 m^3$ of propane supplied:

$$\frac{12 \times 1.1 \times 0.7 \times 10 \times 17}{1000} = 1.58 \text{ kg of 100 per cent } H_2O_2,$$

corresponding to 5.2 kg of 30 per cent H_2O_2 .

Since the reaction product contains about 0.6 mol aldehyde per mol of peroxide, which is changed to about 70 per cent in acid, one can, with the insertion of $100 m^3$ of propane, expect an acid yield of about:

$$\frac{12 \times 1.1 \times 0.6 \times 9 \times 0.7 \times 50}{1000} = 2.5 \text{ kg formic acid (acetic acid)}$$

(The molecular weight of a mixture of formic acid and acetic acid is taken as 50.)

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The yield in hydrogen peroxide with circulation of the reaction gases can be stated only after the conclusion of the semitechnical experiment.

Diagram

Gasuhr	-	Gas meter
Inh 50 l.	-	Volume 50 l.
Pressluft	-	Compressed air
Kühlwasser	-	Cooling water
für	-	for
Dampf	-	Vapor
Nach H_2O_2	-	to H_2O_2 distillation plant
Destillations Anlage	-	at the beginning
Bei Beginn	-	Washing
Waschung	-	Valve
Ventil	-	Reduction
Recluzier	-	Safety
Sicherheits	-	Manometer
Manometer	-	Thermometer
Thermometer	-	Amount measurer
Mengen messer	-	Steam trap
Kondenstopf	-	Recycle pump
Umlauf Pump	-	Liquid stoppage
Flüssigkeitsverschluss	-	Container
Empfänger	-	Peroxide
Peroxyde	-	Liquid
Flüssigkeit	-	Low
Tief	-	Cooler
Kühler	-	Condensor
Kondensator	-	Cooling Surface
Kühlfläche	-	with
mit	-	Separator
Abscheider	-	Air
Luft	-	Cooler (Cooled)
Gekühlter	-	Escape
Austritt	-	out of the reactor
Ausdem reaktor	-	Electric
Elektr.	-	Ignition
Zündung	-	Nitrogen
Stickstoff	-	Surface
Zlasche	-	Oxygen
Sauerstoff	-	Reaction space
Reactionsraum	-	Propane
Propan	-	Layer
Lager	-	Tanks
Tanks	-	Apiece
Je	-	Filling
Füllung	-	

