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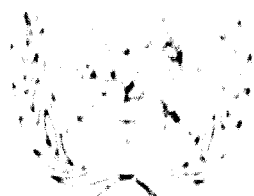
New York

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UNESCO, PARIS, 1971.

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2000

United Nations Industrial Development Organization

RUSSIAN

International Petrochemical Symposium on the
Development of the Petrochemical Industries in
Developing Countries

PERUSSIA

Paris, 1967, 20 - 31 October 1967

SUMMARY

"NEW METHODS FOR THE PRODUCTION OF DIPHENYLPROPANE, DIVINYLBENZENE, GLYCIDOL AND SYNTHETIC GLYCERINE"^{1/}

A. G. Benzailo
USSR

Production of glycerine

A two-stage method for the production of synthetic glycerine from propylene oxide has been elaborated. First stage of the method: isomerization of propylene oxide to obtain allyl alcohol. The yield of allyl alcohol on the converted propylene oxide amounts to 89 %.

Propylene oxide is isomerized to allyl alcohol over a lithium phosphate catalyst containing other ingredients. This catalyst provides for a conversion degree of propylene oxide up to 90 % the selectivity being in the range of 87 - 92 %.

The catalyst capacity amounts to 700 - 800 g/l per hour.

Second stage of the method: synthesis of glycerine from allyl alcohol and hydrogen peroxide. As a result of the interaction of allyl alcohol with hydrogen peroxide in

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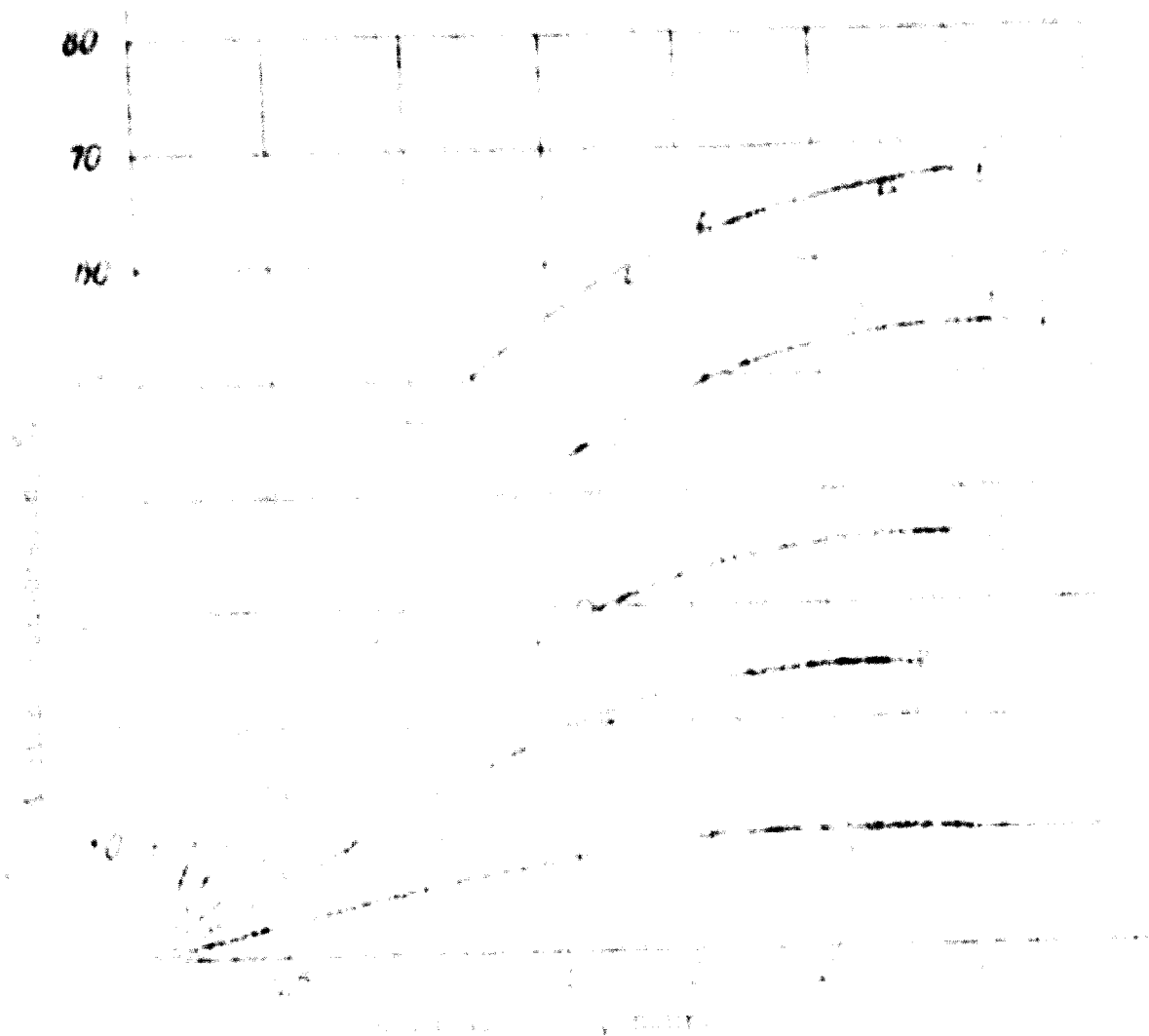


Fig. 1. Dependence of the rate of the reaction on the residence time at different temperatures:
 I - 25°C, II - 30°C, III - 35°C, IV - 40°C, V - 45°C (with the temperature of 25°C).

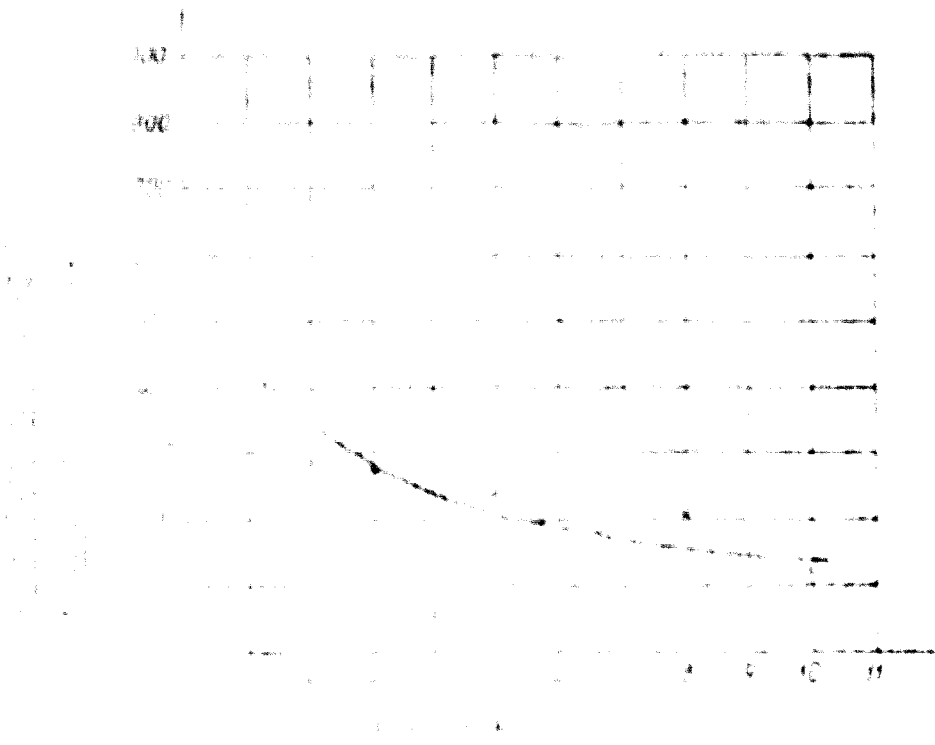


Fig. 2. Effect of reaction temperature on the molar ratio of products formed in the reaction - 75 °C, residence time - 1 hour.

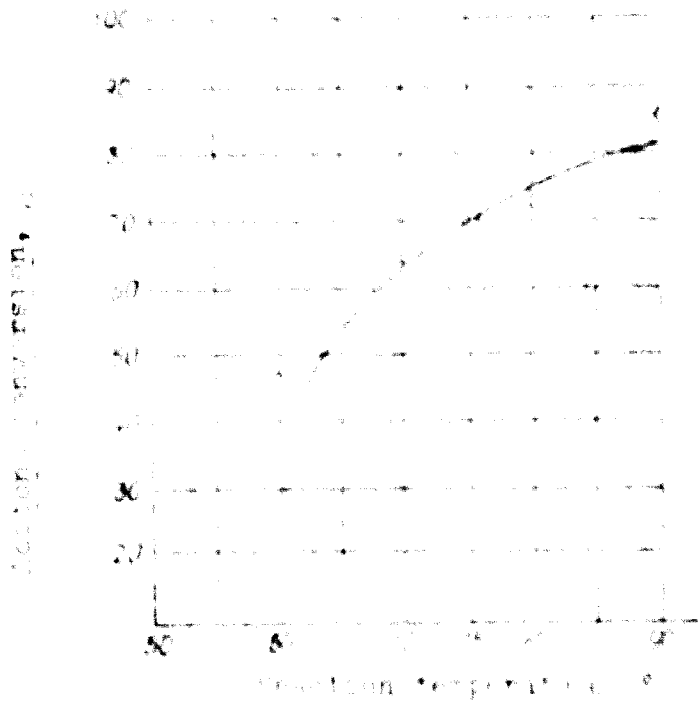


Fig. 3. Effect of reaction temperature on the conversion percentage of acetone over the catalyst at 75 °C, residence time - 1 hour.

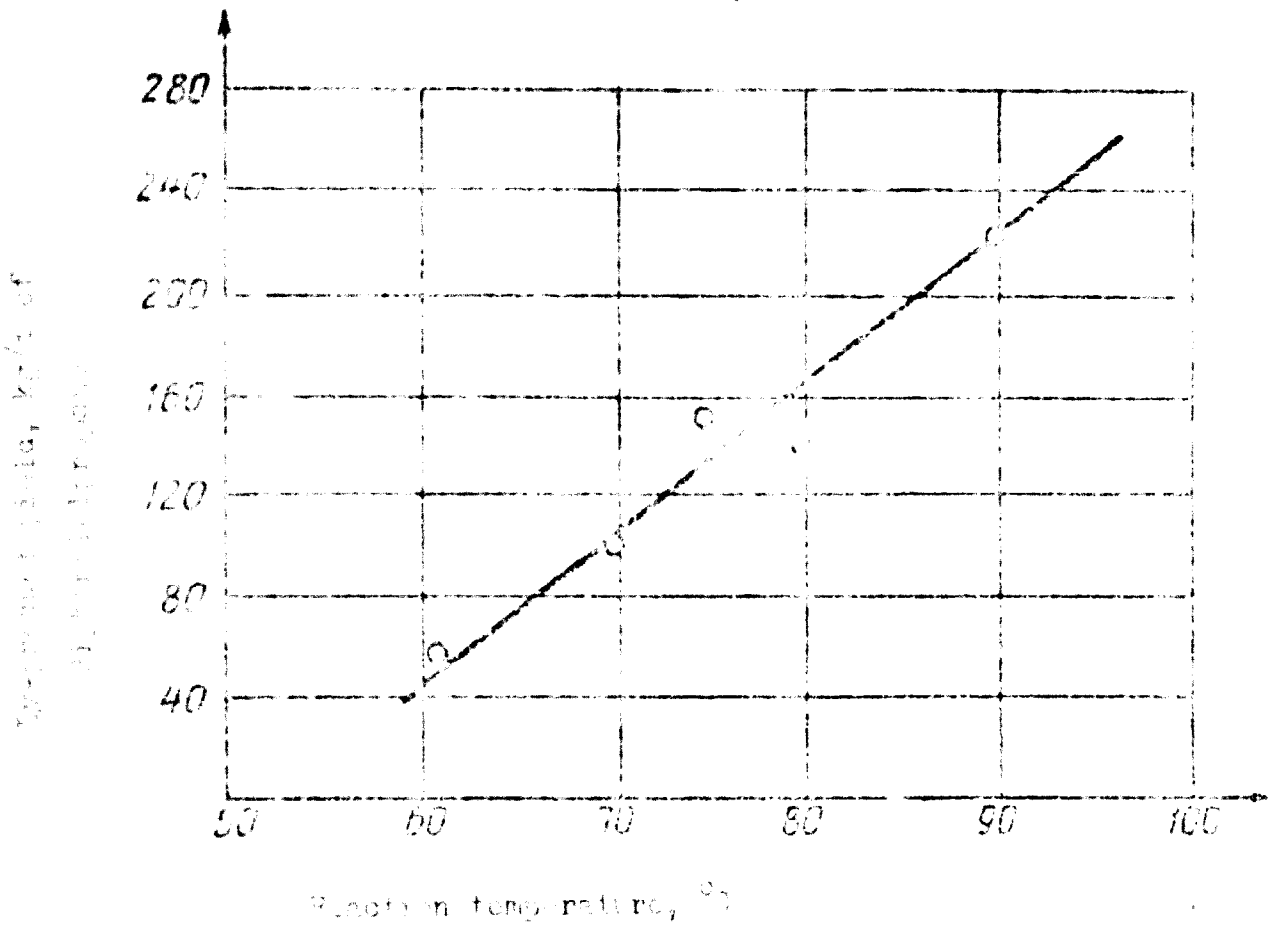


Fig. 4. Variation reaction temperature with by-product formation (molar ratio - 10 : 1, residence time - 2 hours).

Table 1: Productivity of the catalyst with additives.

Additive	Phenol to acetone molar ratio	Residence time, hours	Catalyst productivity, g/1.h.
N 2	5:1	0.48	455
	5:1	0.9	293
	5:1	1.8	170
	10:1	0.95	185
N 1	5:1	0.48	309
	5:1	0.95	194
	5:1	1.9	112

The yield of by-products may decrease greatly due to introduction of additives. For instance, the introduction of additive N 2 (phenol to acetone ratio in feed is 5:1) decreases the yield of by-products from 210 kg/t to 143 kg/t and to 113 kg/t of diphenylolpropane at $V = 10:1$. The diphenylolpropane produced in this case has high quality and properties as follows:

colour	- white
melting point	- 156.5 - 157 °C
content of volatile components	- not more 0.5%
optical density of alcohol solution measured with photocolorimeter -H-57	- 0.05
content of phenol	- not more 0.05%.

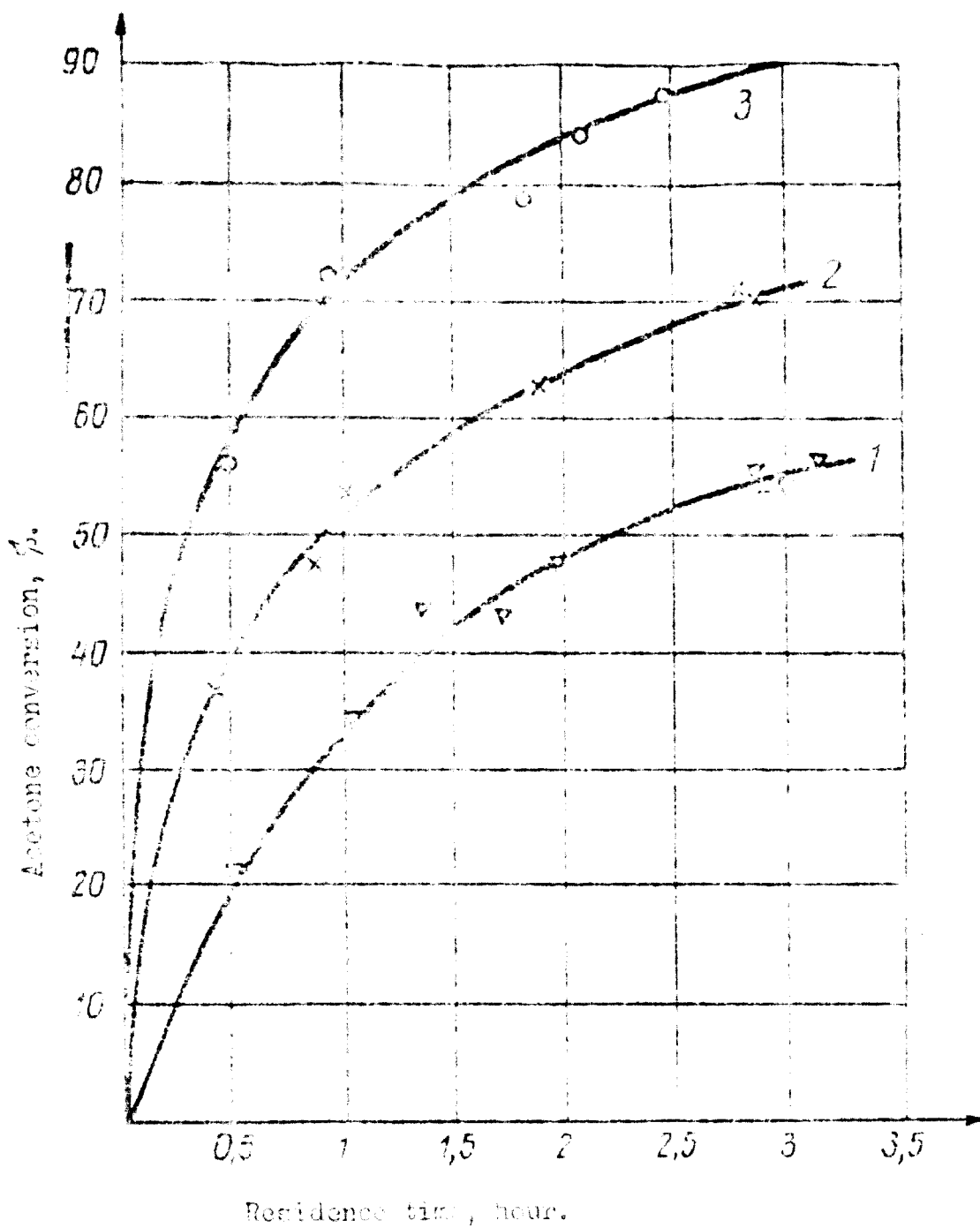


Fig. 5. Variation of acetone conversion with residence time at molar ratio of phenol to acetone in mixture of 5 : 1, $t = 75^{\circ}\text{C}$.

1. Without additive.
2. With additive I 1.
3. With additive II 2.

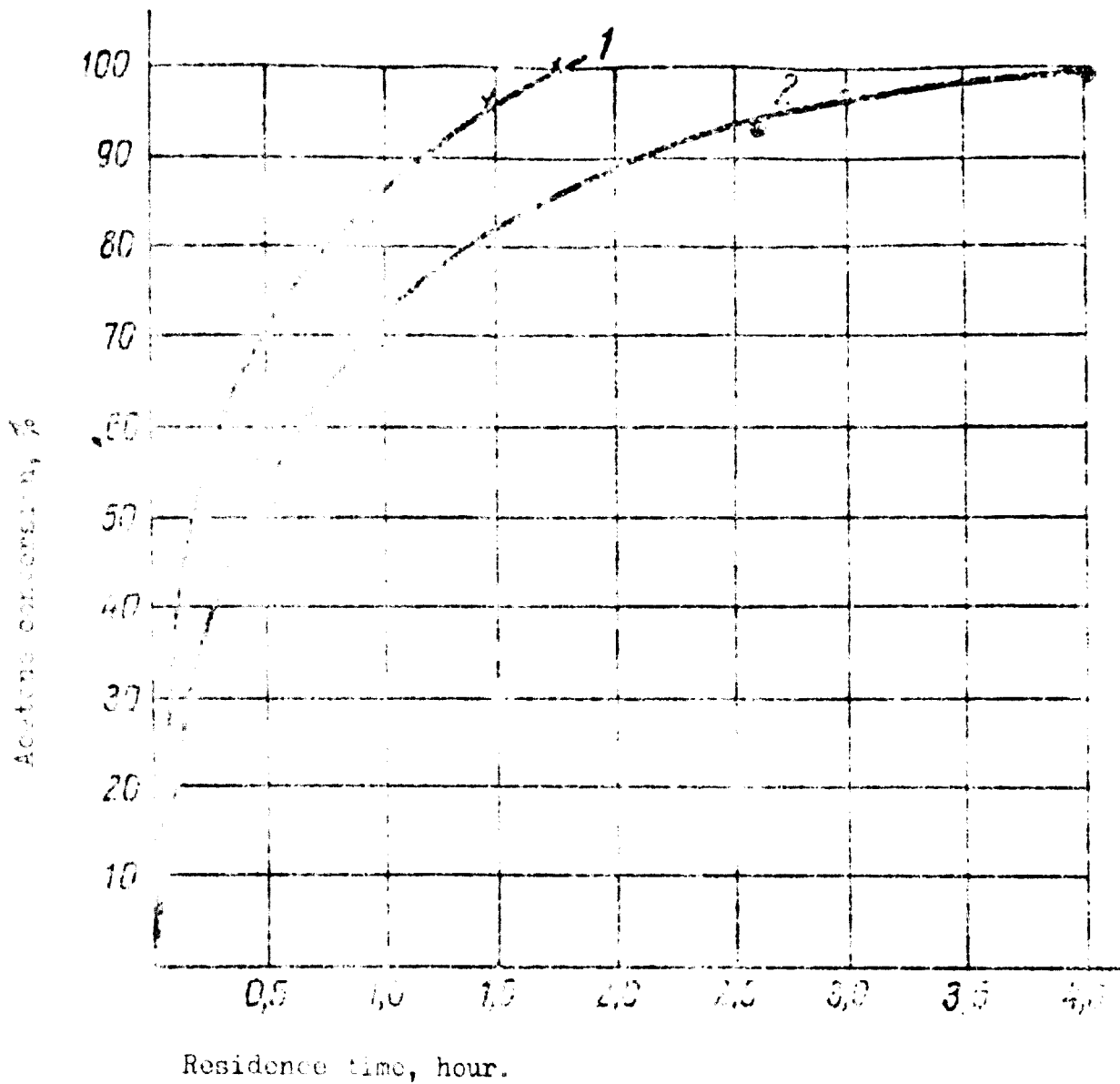


Fig. 6. Variation of acetone conversion with residence time for mixtures at molal ratios of 5 : 1 and 10 : 1 with additive N₂ at $t = 75^{\circ}\text{C}$.
 1 - 10 : 1, 2 - 5 : 1.

Thus, the synthesis of diisobutylene over ion exchange resins with conditions given the following advantages:

1. The amount of diisobutylene obtained in few days is comparable with that obtained in several months when the sulfuric acid catalyst is used and the amount of diisobutylene is small.
2. Higher yields of diisobutylene can be received resulting in the reduction of its consumption and in the size of the reactor.
3. The yield of diisobutylene increases.
4. High quality diisobutylene is produced.

According to our method diisobutylene is synthesized over cation exchange resin in the presence of some additives and excess of phenol in comparison with the steric hindrance amount.

90-95% conversion rate at 100°C per pass and a catalyst circulation rate of 10-15 times is required.

The operational life of an ion exchange resin till regeneration required is not less than 2000 hours.

The consumption rate of additives in all stages they can be reduced. Phenol, generated, is distilled and recycled. Low diisobutylene product yield is always easily separated from impurities by precipitation from solution. The flow diagram of the process is simple and it is easy to operate.

This process will permit a production of diisobutylene by continuous processing on a large scale through automation of the process as a whole.

As to our method, the production cost and capital investments of diisobutylene can be much lower than in the case of production with the help of sulfuric acid and hydrogen chloride.

For instance, according to our method capital investments per unit are only 30% and production cost are 10% lower than in production with help of hydrogen chloride. In comparison with the sulphuric method, the savings obtained may be much more substantial.

II. Production of meta- and para-divinylbenzenes of high quality.

Divinylbenzene is an important chemical used in organic synthesis.

Divinylbenzene may copolymerize with other vinyl compounds to form copolymers of a certain structure that can have wide applications.

Divinylbenzene is applied mainly in the production of ion exchange resins. The best grades of ion exchange resins can be synthesized as copolymers of various monomers with divinylbenzene. These ion exchange resins are applied for complete demineralization and purification of water, for the treatment of waste water, for removing metals from waste water, for the water treatment, as catalysts, in food and medical industries, etc. The present ion exchange resins are applied on a commercial scale in the production of uranium from lean ores containing less than 0.5% of uranium.

The method of purification of antibiotics and other medicines with the aid of ion exchange sieves is applied to a great extent.

The kind of styrene used in this case may be varied by variation of styrene to divinylbenzene ratio in the initial copolymer.

The copolymers of styrene and divinylbenzene macro-porous ion exchange resins, used for adsorption of organic compounds of higher molecular weight can be produced.

Divinylbenzene may be used as a main crosslinking agent in the preparation of various resins for special applications.

Resins prepared by copolymerization of monomers with divinylbenzene are characterized by higher thermostability, lower solubility, good chemical stability and better insulating properties.

Divinylbenzene may be used for improving the physical and chemical properties of elastics, rubber, man-made leather, organic dielectrics, etc.

Divinylbenzene added at an amount of 0.5 parts by weight makes it possible to treat JI rubber in both calender and press because of decrease of shrinkage of samples from 43 to 9%, swelling from 54% to 15% and also gives improved ageing resistance to the rubber.

Divinylbenzene is produced by a method of catalytic dehydrogenation of diethylbenzene in the presence of steam at a temperature of 600 - 650 °C which results in the formation of a mixture containing 15 - 25% of divinylbenzene and 75 - 85% of diethylbenzene, benzene, toluene, styrene, ethylvinylbenzene, etc. It is very difficult to separate pure divinylbenzene from this mixture because its components may form polymers readily. That is why, on a commercial scale, only a part of the divinylbenzene is rectified (up to 45 - 55%) in a complicated column.

American "Dow Chemical" and English "Light Oil" are producing 50 - 55% divinylbenzene maxima which contains, together with mixed divinylbenzene isomers, from 5 to 12 different compounds.

The method of catalytic dehydrogenation is characterized by substantial high consumption of starting diethylbenzene due to low selectivity of the process, lower content of divinylbenzene in mixture (15 - 25%) and troubles which occur in the course of divinylbenzene concentration.

Investigations on creating an improved method of dehydrogenation of diethylbenzene to divinylbenzene have been carried out in various countries but, so far without any substantial results.

Divinylbenzene is produced in the course of a complicated reaction of catalytic dehydrogenation in two stages with the intermediate, ethylvinylbenzene, being formed while by-products are formed at each stage:

Diethylbenzene ----- ethylvinylbenzene ----- divinylbenzene.

Now it is not possible to separate divinylbenzene from by-products produced in the dehydrogenation of diethylbenzene by any economic method and this results in divinylbenzene of low quality and a high consumption of materials per ton of production.

For some years, Scientific Research Institute of Synthetic Alcohols and Organic Products has investigated a commercial method for the synthesis of divinylbenzene of high purity based on a new principle.

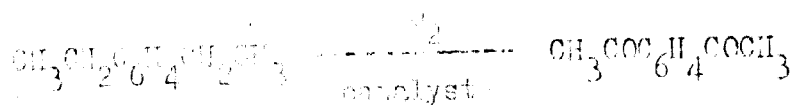
We are producing divinylbenzene by reactions with higher conversion and selectivity which permit either to avoid or to simplify the separation of compounds which polymerize and deteriorate readily.

This method provides for producing separated isomers of divinylbenzene of high purity.

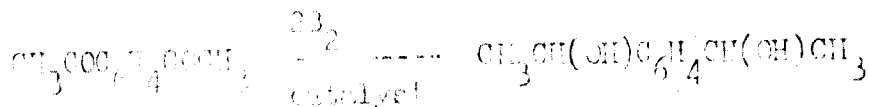
Diethylbenzene, formed together with ethylbenzene in the course of alkylation of benzene with ethylene in accordance with Friedel-Craft reaction in the presence of aluminum chloride as a catalyst is used in our process as a starting material. In this case, diethylbenzene is formed at an amount of 25 - 32% of ethylbenzene weight.

Divinylbenzene production according to our method may be described as follows:

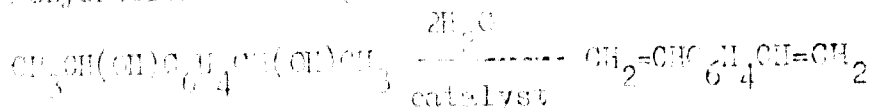
1. Oxidation of diethylbenzene to diacetylbenzene.



2. Reduction of diacetylbenzene to bis-(α -hydroxyethyl) benzene



3. Dehydration of bis-(α -hydroxyethyl)-benzene to divinylbenzene.



Diethylbenzene is oxidized to diacetylbenzene in the liquid phase by oxygen or gas containing oxygen in the presence of salts of metals with transient valence (cobalt chloride in the main). Diethylbenzene is oxidized to diacetylbenzene under mild conditions at a temperature 110-130 °C giving a high conversion of (6-75%).

We have investigated various methods of the reduction of diacetylbenzene to bis-(α -hydroxyethyl)-benzene such as Meerwein-Ponndorf reaction in the presence of aluminum isopropylate catalyst and isopropyl alcohol donor, reduction with hydrogen over heterogeneous commercial catalyst (Raney nickel and nickel-chromium catalyst in suspended bed).

According to our method, diacetylbenzene is reduced with help of all said methods in such a selective way that compounds obtained after hydrogenation contain up to 97 - 99% of bis-(α -hydroxyethyl)-benzene and can be passed to next stage without additional purification and rectification.

We have investigated a method of hydrogenation of diacetylbenzene in liquid phase over nickel-chromium catalyst in fixed bed. However, this method gives lower selectivity than in the case of hydrogenation of diacetylbenzene over nickel catalyst in gas phase. The content of divinylhydrocarbons in the reaction mass obtained in the course of hydrogenation of diacetylbenzene in a fixed bed is not more than 92 - 94%. For recovery of pure 1,4- and 1,3-divinyldibenzene it is necessary to distill the reaction mass at a reduced pressure of 0.5 mm Hg.

1,4-Divinyldibenzene or divinylbenzene is dehydrated over magnesium sulphate which enables for a very high selectivity of the reaction. The content of divinylbenzene in the reaction mass reaches 98%.

Divinylbenzene can be separated from impurities (of diacetylbenzene and 1,4- and 1,3-divinyldibenzene) by simple distillation under vacuum.

Various inhibitors necessary for storage of concentrated divinylbenzene have been investigated and p-nitrophenol has been found to be best because it prevented diene polymerization during for 40 days at a temperature of 20°C.

Methods of analytical analysis which permit the determination of purity and exact composition of starting, intermediate and final products have been developed.

Samples of divinylbenzene prepared have been tested successfully in some research institutions. Economic analysis of various methods for the production of divinylbenzene shows that according to our method the production cost and energy investment are only half the projected values for the production of divinylbenzene by dehydrogenation, and a quarter of the practical values in existing commercial production of divinylbenzene.

Diethylbenzene which in the production of divinylbenzene is produced as a by-product in the course of alkylation of benzene with ethylene and consists of 60% of meta-isomer, 10% of para-isomer and 10% of ortho-isomer.

Relationship of reflux ratio with the number of theoretical plates at a given separation rate obtained in the course of computation has shown that rectification of starting diethylbenzene increases the production of

... fraction rich in p-diethylbenzene only. The distillate is passed into distillate together with residual m- and o-diethylbenzene. This is done because boiling points of o- and m-diethylbenzene are close to each other.

The p-diethylbenzene is separated from the p-isomer at the stage of crystallization. However, in this case diethylbenzene is separated at the first stage ethylacetophenone is formed and at the second stage ethylacetophenone is separated.

Diethylbenzene is readily separated from mixed isomers by crystallization. The m- and o-diethylbenzene is a product of high purity. The difference in melting points of isomers is used for separation (m- +111 °C, meta- +32 °C, ortho- +39-40 °C).

The m- and o-diethylbenzene is separated by the crystallization method. The m- and o-diethylbenzene is separated with each impurities as ortho- and meta-diethylbenzene.

Diethylbenzene is separated by a combined method of distillation and crystallization. The final purification of the product is done by crystallization.

The final purification of diethylbenzene aimed at separation of m- and o-diethylbenzene from the product of p-diethylbenzene is performed in a column with two columns, the first one being for separation of m- and o-diethylbenzene. p-diethylbenzene is separated in a second column having such parameters as:

- number of theoretical plates - 187
- efficiency - 93
- vertical position - 200 mm Hg
- top temperature - 134 °C
- bottom temperature - 165 °C.

98% pure p-diethylbenzene is obtained as a distillate and 26% of m- and o-diethylbenzene, 50% of p-diethylbenzene and ortho-diethylbenzene - as follows.

Pure m-divinylbenzene is produced from pure isomer and pure polyvinyl benzene by oxidation of the latter with consequent separation by extraction of the insoluble polyvinylbenzene.

Also, as indicated, it may be obtained in another way by oxidation of mixed diethylbenzene isomers, i.e., m-xylene, in which a mixture of pure m-xylene and benzene is used as the starting mixture. However, divinylbenzene isomers are hard to oxidize and the resulting products were even then, m-dioxybenzene and m-dioxytoluene.

In the course of the investigation a number of samples of divinylbenzene with the following properties have been obtained:

Receiving number 100000000 as a sample with specific colour when crystallized at low temperatures at a temperature of 29-30°C, refractive index $n_D^{20} = 1.5125$. According to literature melting point is +31°C and refractive index $n_D^{20} = 1.5126$.

Receiving number 100000000 as a sample, colourless liquid with specific colour, refractive index $n_D^{20} = 1.5135$. According to literature refractive index of m-divinylbenzene is $n_D^{20} = 1.5135$.

A mixture of m-xylene isomer and m-dioxytoluene with refractive index $n_D^{20} = 1.5135$.

Thus, it may be seen with existing methods of divinylbenzene production the method devised by scientists of our Institute for Synthetic Alkyls and Organic Chemistry is characterized by the following features:

1. Higher purity of final product which reaches 99%.
2. Separation of divinylbenzene isomers as well as mixed ones may be prepared.
3. Better economical situation because the consumption of starting diethylbenzene is a great deal smaller if it is in the process of catalytic dehydrogenation of diethylbenzene to 2 t.

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We have chosen a catalyst consisting of lithium phosphate combined with other components (up to 50%), which gave substantially increased service life and operating cycle for the catalyst.

This catalyst was tested for its service life on a laboratory and pilot scale and with the help of a part of the reaction apparatus which was intended to apply in future for a commercial plant (tube of 3 m in height, catalyst volume 730 ml).

In this case the products listed below were formed as by-products:

Propionic aldehyde	5.6 % by weight
Acetone	3.0 - " -
N-propanol	1.25 - " -
Acrolein and non-identified compounds	1.15 - " -

Allyl alcohol of the following composition was formed:

Allyl alcohol	more than	98 %	by weight
Propionic aldehyde			traces
Acetone			traces
N-propanol		1.5%	by weight.

Consumption of raw materials per 1 t of 100% pure allyl alcohol:

1. propylene oxide (100%)	1.14 t
2. catalyst	0.45 kg

Wastes.

100 kg of propionic aldehyde mixed with acetone are formed in the process (propionic aldehyde to acetone ratio is 2:1).

The production of glycidol and glycerine from allyl alcohol.

A method of the production of glycerine from allyl alcohol and hydrogen peroxide in the presence of tungstate catalysts including process of separation and purification of the product, preparation and regeneration of the catalysts was investigated on a laboratory scale and then checked and tested on a pilot plant scale.

Initially a tungstic acid catalyst. 30% aqueous solution of allyl alcohol and hydrogen peroxide at a molar ratio of 1:1.04. Reaction time 10 hours in the presence of tungstic acid at amounts of 0.5 g/l. of the reaction media.

Unreacted allyl alcohol and unreacted hydrogen peroxide were removed from the reaction media by a distillation process. The catalyst was regenerated. Then the product was separated and distilled. The yield of allyl alcohol was 95% with respect to the allyl alcohol and 90% with respect to the hydrogen peroxide.

The process of production of glycerine was tested on a pilot plant. The results obtained were in full analogy with the results of the design for a continuous process.

A major disadvantage of the catalyst is the necessity of regeneration. This is done by a process which results in a loss of catalyst. The amount of catalyst in the reaction media is 0.5 g/l.

In order to avoid this disadvantage we have chosen a new catalyst. This catalyst is made of other chemicals usually used in the chemical industry.

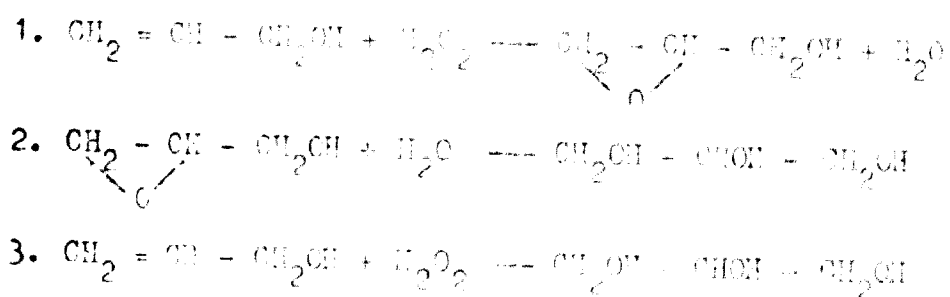
The catalyst is easily separated from the reaction media and it is not necessary to regenerate it. The application of this catalyst is a process of catalyst regeneration, regeneration of the catalyst, flow material and reagents and the catalyst is not contaminated with organic substances.

A method for the production of synthetic glycerine from allyl alcohol and hydrogen peroxide in the presence of our catalyst consists of stages as follows:

1. Reaction of allyl alcohol with hydrogen peroxide to form glycidol-glycerine mixture.
2. Recovery of unreacted allyl alcohol from the reaction media and its purification.
3. Catalytic hydrolysis of the glycidol in the reaction media to obtain glycerine.
4. Concentration by evaporation of glycerine solution.

Allyl alcohol reacts with hydrogen peroxide in the presence of a heterogeneous catalyst. The epoxidation of allyl alcohol to glycidol proceeds, in general, under recommended conditions. Small amounts of glycerine (1 mole per 25 moles of glycidol) present in the reaction media are formed as a result of various hydration of a parallel reaction of hydroxylation of allyl alcohol to glycerine.

These reactions may be described by equations as follows:



In order to increase glycidol yields and avoid the side reactions of oxidation the reaction of epoxidation is preferably conducted under mild conditions such as a temperature below 70 °C and at a selected reagent-to-reagent ratio.

Selectivity of the epoxidation increases as allyl alcohol to hydrogen peroxide molar ratio increases.

Glycidol is hydrated to glycerine directly in the reaction media without separation.

Glycidol reacts with water as follows:



Higher yields are obtained if it is necessary for this product to be purified. The process proceeds at normal pressure and at 100°C temperature in the absence of catalyst or without it.

Distillation of the product yields grade to technical grade glycerine. In order to obtain higher grades, purified the usual methods in order to obtain the required quality.

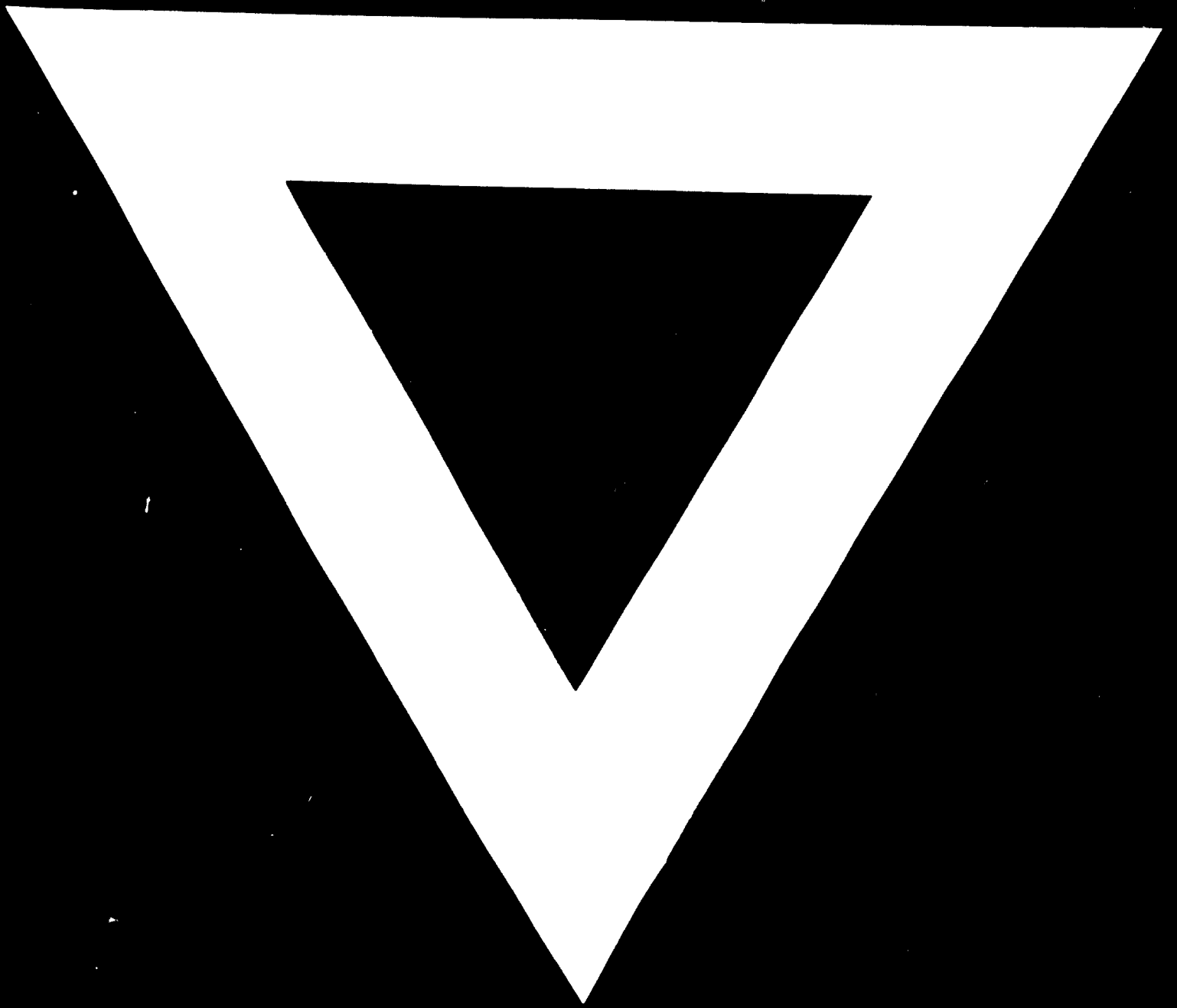
Experiments show that the products prepared by this method are:

1. Acid value (mg KOH/g)	not less 1.2584
2. Alkalinity (mg KOH/g)	not less 99%
3. Specific gravity	not more 0.01%
4. Viscosity (at 20°C)	not more 0.01%
5. Free water	- none
6. Free alkali	- none
7. Chloride (mg/g)	- not more 0.7 mg KOH

Consumption of reagents for the production of 100 kg of distilled glycerine:

Reagent	unit	Consumption rate
1. Glycerol	t	0.77
2. Hydrochloric acid	t	0.45
3. Catalyst	kg	2.0 - 1.0





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