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TRANSLATION OF PAGES 1292-1301  
OF TECHNICAL OIL MISSION  
MICROFILM REEL NO. 14

Main Laboratory  
Division: Experiments  
A.N. 111/42

00001292-3  
Leuna Werke,  
December 3, 1942  
Ba

Bag 3043. Target 30/4.02

FILE NOTE

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Re: Dehydrating Catalysts for Butadiene Production  
Discussion in Schkopau November 26, 1942

Present: Dr. Breners } Dir. Dr. Herold } Leuna  
          Dr. Kleine } Schkopau Dr. Noirotsung }  
          r. Broich }

In experiments relating to the splitting of dimethyl dioxane to isoprene,  $\text{CH}_2\text{O}$  and  $\text{H}_2\text{O}$ , considerable difficulties have been encountered in Leuna, insofar as the catalysts become entirely inactive through carbonization in a very short period of time and the ovens are clogged through deposition of resin. Since Schkopau has had experience, dating several years back, in this field through work on the dehydration of 1,3-butylene glycol to butadiene, the methods of operation utilized there were to be used in the Leuna experiments.

Catalyst (contact):

In Schkopau it was found that only phosphoric acid-containing catalysts can be used; other catalysts are entirely inactive. The phosphoric acid catalysts in Schkopau cannot be regenerated. They consist of graphite as carrier, containing from 5 to 10 per cent of sodium pyrophosphate, 3% of free phosphoric acid and 30% of dimeric sodium metaphosphate, and some butylamine. According to the experience gained in Schkopau the catalyst must not contain more and not less than 3-4% of free  $\text{H}_2\text{PO}_4$ . The catalyst must be, as far as possible, of a fine crystalline nature. A sample of this catalyst will be tested in Leuna for splitting dioxane. Besides, Schkopau will put its experience in the analysis of such complex phosphoric acid catalysts at the disposal of the Leuna catalyst division.

Procedure:

In Schkopau the glycol is passed with  $\text{H}_2\text{O}$  (1:1 pts. wt.) at  $270^\circ\text{C}$ . over the catalyst. 20 to 30 cc of glycol is sprayed in for 1 liter of the catalyst. At a higher throughput the catalyst becomes exhausted too rapidly and the yield is poorer since the consumed catalyst is conducive to side reactions. For this reason the glycol in industrial operation is sprayed in through lateral nozzles at different heights of the catalyst layer in order to shorten the contact time with the spent catalyst.

In the splitting of glycol a 100% conversion must be aimed at, because the separation of  $\text{H}_2\text{O}$  and glycol is too expensive. In the splitting of dioxane, however, a partial conversion is acceptable, and this would be favorable for the yield. The danger of gumming (resinification), on the other hand, is greater in the dioxane splitting since, in addition to isoprene, extremely reactive  $\text{CH}_2\text{O}$  is produced. This observation was also made in Schkopau in experiments relating to the splitting of butylene glycol-acetaldehyde-acetal where the catalyst was also resinified in a few days.

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Since, under these conditions, the way to isoprene through the splitting of dioxane must at present still be considered as very difficult, Dr. Breuers proposes to split the dioxane under pressure to methanol and 1,3-amylene glycol, a reaction which has led to satisfactory results with similar compounds. Should this be possible, the 1,3-amylene glycol could be treated exactly in the same manner as 1,3-butylene glycol, which is now a technically completed process. The gentlemen from Schkopau have assumed the responsibility of carrying out experiments on destructive hydrogenation of dioxane. For this purpose, dioxane samples are currently being sent to Schkopau.

In addition to the usual ovens, annular iron ovens of 2.5 liters capacity are being used chiefly heated with saltpeter which provides a uniform temperature supply and owing to their size also allow definite estimates of the yield. Such an oven will also be installed in Leuna.

#### Purity of Isoprene:

Isoprene suitable for polymerization must above all be characterized by highest purity. While hydrocarbons up to a content of 1-2% do not have any noticeably harmful effect, the presence of compounds with active groups, such as alcohols, aldehydes, and ketones must be painstakingly avoided. For isoprene, methanol and formaldehyde are particularly to be considered among such compounds. Methanol must not be present in quantities higher than 0.01% and  $\text{CH}_2\text{O}$  not higher than 0.001%, which, in addition to fractionation, would require a combined water and alkali wash.

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Buna Werke  
G.m.b.H.  
Attention: Dr. Breuers

00001294  
Dr. Herold

Schkopau (Merseburg)

Nitrogen Division Feb. 8, 1943

Dehydration Catalysis

During the discussion in Schkopau November 26, 1942, you kindly offered to carry out experiments with our dimethyl-1,3-dioxane involving its destructive hydrogenation to amylene glycol since great difficulties have been encountered by us in the direct splitting to isoprene, owing to resinification of the catalyst and its resultant short life.

Meanwhile we have succeeded in finding  $H_2PO_4$ -containing catalysts which can be regenerated so that the above difficulties should now be considered as overcome. The consumption of catalyst, referred to isoprene, amounts to 1.3-2% in small experimental ovens. Under these conditions it no longer appears necessary to pursue the roundabout way over amylene glycol and to bother you with experiments made in this direction. We would greatly appreciate a report of your past results on destructive hydrogenation so that we may once again check and compare the two methods of reaction.

In compliance with your wish we shall send you in due course a sample of our catalyst. We have had no success with your "acetal catalyst."

At the same time we wish to ask you if we may send you another 3-4 kg. of isoprene for testing, having been purified, in addition to distillation, also with a water and alkali wash to remove formaldehyde and methanol.

Finally, we acknowledge receipt of the butadiene-containing butene which is now free of resin. After completion of alkylation experiments therewith, we shall communicate the result to you at once.

Heil Hitler!

(Signatures)

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00001295

Received February 27, 1943  
Nitrogen Div. 0058  
Bag 3043, Target 30/4.02  
Ammonia Plant (Merseburg)  
G.M.b.H.

Buna-Werke  
G.M.b.H.

Nitrogen Division

Leuna-Werke through Merseburg

Schkopau  
through Merseburg  
February 23, 1943

Dehydration Catalysis

You informed us that you had succeeded in finding a phosphoric acid-containing catalyst that can be regenerated and with which the splitting of your dimethyl-1,3-dioxane to isoprene proceeds satisfactorily. We particularly appreciate this finding inasmuch as we have been unable to find a suitable way to isoprene by means of destructive dehydrogenation of your dioxane. In a few experiments we tried to obtain an explanation for these causes. We ascertained that the formaldehyde-acetal of the 1,3-butylene glycol can be quantitatively split to 1,3-butanediol and methanol, although with greater difficulty than the corresponding acetaldehyde-acetal. In the destructive hydrogenation of your dioxane under identical conditions, practically no methyl butylene glycol was obtained, but mainly oily products of a very wide boiling range. In a special experiment a ring acetal was subjected to destructive hydrogenation, having been obtained by synthesis from 3-methyl-butanediol-1,3 and formaldehyde. In the reaction products a considerable amount of 3-methyl-butanediol-1,3 was recovered, in addition to oily products and partially unchanged ring acetal. We conclude from these results, which are somewhat contradictory to the results obtained in the splitting of your dioxane, that the dimethyl-1,3-dioxane supplied by you still contains impurities which in some form or other disturb the liberation of 3-methyl-butanediol-1,3. On the basis of these results our intention is not to pursue this problem any further.

In your aforementioned letter you asked us to return a sample of your phosphoric acid-containing catalyst which can be regenerated. Since the sample has not yet been received, we question whether it has actually been sent by you.

Buna-Werke

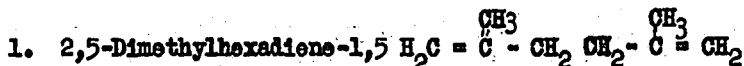
G.M.b.H.

Dr. Farnwitz  
Tech. Lab. B 30  
Div. P

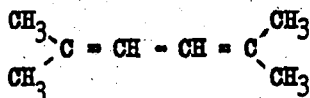
Schkopau  
January 5, 1942

Polymerizability of 2,5-Dimethylhexadiene-1,5 and Tetramethylbutadiene

We received from Leuna 2 conversion products of isobutylene to be tested for polymerizability, under the following designations:

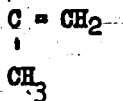


2. Tetramethylbutadiene (obtained by Isomerization of 1)



The present rating was done in the monthly reports of August and September. The following is given as a summary report of the investigations made by Dr. Meyer and Dr. Johne in the P-Laboratory: Dimethylhexadiene was redistilled accurately prior to the experiments. B.p. 113°C. (uncorr.), small amounts of first runnings, 10% residue. For determining the iodine number (Dr. Johne) the substance was titrated with Wijs iodine solution. In 100 g. of substance, 1.84 mol. double bond was found, corresponding to 2.02 double bond per mol. substance.

A perbenzoic acid titration (Dr. Meyer) gave almost exactly the same curve as for diisobutylene. It may therefore be assumed that the double bond is substantially located in a terminal position, of the type



The grouping  $\text{CH} = \overset{\text{CH}_3}{\text{C}}$  may also be present, up to a certain percentage,

as in diisobutylene. Ozon splitting is still to be made.

No reaction took place with sodium. In accordance with our frequent findings that copolymerization with butadiene, when possible, proceeds best in a molar ratio of 1:1, owing to special conditions of activation, the addition of emulsifier A in the state of emulsion was tested in the phase of 100:115 at 50°C. within a period of 48 hours. The presence of the Leuna hydrocarbon partially inhibits polymerization. The yield, referred to the butadiene supplied, was 100% of the theoretical yield; the hexadiene could be recovered to the extent of 80% by steam distillation. Consequently, no copolymerization of hexadiene had taken place.

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The tetramethyl butadiene was used without previous distillation. 1.1 mol. double bond was found for 100 g. substance with Wijs iodine solution (Dr. Johns) corresponding to 1.2 mol. per mol. substance.

No Diels reaction occurred with maleic acid anhydride, only a slight resinification.

Titration with perbenzoic acid (Dr. Meyer) should indicate only 1.1 double bond owing to probable steric hindrance through the primarily formed ethylene oxide group. However, an entirely different conversion took place.

After fifteen minutes 112% of the theoretical double bond yield was obtained. The value was not constant but changed to 176% in 23 hours, rising to a final value of 182% of the theoretical value. From this behavior it is consequently not possible to draw any conclusions as to the constitution of the hydrocarbon.

With  $1/2$  and 1% of sodium no polymerization was observed between 35 and 50°C. in fourteen days. In admixture with butadiene the latter polymerizes alone.

With boron fluoride etherate only an increase in viscosity was noted, and this first on heating the two substances.

A similar mixture, as previously described for hexadiene, was polymerized at 55°C. in emulsion. After 48 hours only 5% of the butadiene was polymerized. The hydrocarbon was recovered to the extent of 97.5%. The general appearance was that the substance still contained a compound which inhibited polymerization. The variable results in the addition of iodine and in the titration with perbenzoic acid also indicate a lack of homogeneity.

/S/KI /S/ Pannwitz

**Restricted**

Dr. V. Staden

00001297 - 1300

August 25, 1942

Experimental Plant for Methylated Butadienes (Mesoprene Experiments)

For the tentative report which you have accepted, relative to tentative experiments on a large scale in the G. B. Chem., the following data may serve as a foundation, which will be presented by Dr. Elbel in a letter to the Office, provided you have no objections or wish any changes.

The problem of producing an adhesive rubber synthetically has again become the focal point of interest and is the goal of much experimental work.

It can be made from isoprene as well as on the basis of the old Hofmann diene (2,3-dimethylbutadiene) synthesis.

The problem of suitable producing methods has now become a pressing matter for both of these olefins.

A reaction described long ago in the literature and recently resumed in several I. G. plants appeared to offer a satisfactory basis. The problem relates to the condensation of olefins with 2 mols. of formaldehyde to cyclic ethers (methyals from alkylated 1,3 propanediols) (formation of so-called 1,3-dioxane) which may be degraded catalytically by splitting off one mol. of formaldehyde and water to form diolefins. So far the operating laboratories have not succeeded in developing this reaction to an industrially applicable procedure.

On the basis of experience gained in the treatment of particularly reactive raw materials in the development of the alkylation process (AT 244-production) for producing isooctane fuels, we have thought that the application of this experience to the present problem might serve in its development to work out an industrial process.

We, therefore, attacked the problem in the fall of last year and operated, as the work on the alkylation process neared its conclusion, from the Spring of this year with added effort. The problem was developed in this time to the point of establishing the basis for an industrially workable procedure, both for the manufacture of isoprene and of methylisoprene (1,3 dimethylbutadiene).



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The raw materials, in addition to formaldehyde, which can be used as a formaline solution as well as in the form of paraformaldehyde, are isobutylene, and amylene. Both are intended to be produced from the corresponding alcohols derived from the isobutyl oil process by catalytic dehydration. For the first (isobutylene) there are already industrial plants in existence (MT 100-production). The dilute isobutylene from the catalytic dehydrogenation of the T 52-process is also suitable. The additional isobutane does not affect the condensation process and can subsequently be easily removed by distillation.

Amylene can also be prepared by partial hydrogenation of isoprene so that both aforementioned diolefins can be produced from isobutyl alcohol or from isobutane. The yields of both processes are now within 85-80% and may still be increased.

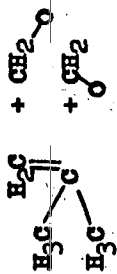
The costs are low, owing to the simplicity of the operation. For checking and providing equipment for previous findings (several paragraphs illegible)

In full operation the plant will presumably have an operating capacity of 30 tons per month.

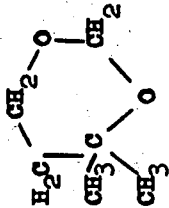
The amount of isoprene or methylisoprene produced, which initially will be much lower than these figures, may be used for industrial operating tests in the adjacent plant of Schkopau and the rubber-technical division of Leverkusen, where interest has been displayed in this problem.

This work is of particular significance for the further development of our branch plant in Auschwitz in which all preliminaries are completed for the adaptation of previous experience which may be of use both with respect to raw materials (isobutyl oil production) and with respect to further work (rubber production).

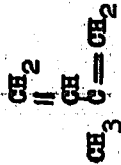
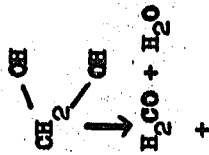
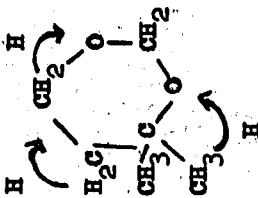
Reaction:



Polymerization  
with  $\text{H}_2\text{SO}_4$



Splitting with  
 $\text{NaH}_2\text{PO}_4$

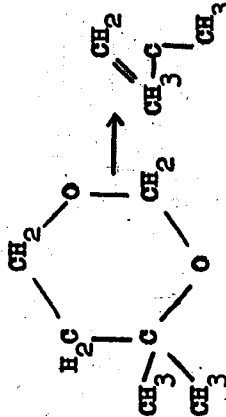


Isoprene

Isobutylene + Formaldehyde

→ Dimethyl Dioxane

II



i-butylene formaldehyde

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Yields:

- Polymerization Isobutylene: 85-90% of the isobutylene supplied converted to m-dioxane  
 " " " " " " higher polymerisates  
 Formaldehyde: 80% " " " " " m-dioxane  
 20% " " " " " is lost
- Splitting: From 100 tons of dioxane supplied, there is obtained 40 tons split. 60 tons remaining unconverted  
 From the 40 tons of converted dioxane  
 95% are split to isoprene + formaldehyde + water according to I  
 5% to isobutylene + formaldehyde according to II