

The Texas Company 3

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TOM REEL 134, SECTION VII, ITEM 1

Assignment : 813

Subject : The Effect of Carbon Monoxide and Hydrogen on Olefins
(Oxo-Reaction)

In Charge : Gemassmer, Berg.

Situation as of 1 October 1944

The report covering the research carried out from 1 April 1944 on, unfortunately was destroyed on May 12th. In the present report we have therefore incorporated all the work covered since February 1, 1944.

Oxation of i-nonylene from Uerdingen.

Pure, intermediate chain length alcohols may be of interest in the preparation of p-oxybenzoic acid ester; Uerdingen (*) expressed the wish to manufacture i-nonylene (propylene polymerisate) over the oxo fraction of a rather large quantity of i-decyl alcohol.

Several pilot experiments were made in the autoclave and then about one ton of i-nonylene was prepared in the oxo-plant from ten experimental batches. The results obtained may be briefly summarized as follows:

Technical i-nonylene (boiling range: 130-160°C.) may be 75% oxated; in this process, large amounts of 60% monomeric i-decyl alcohol are formed. By distillation, the i-decyl alcohol can be separated, with a degree of purity exceeding 95% (boiling range:

(*) Probably the name of a locality where a chemical plant was being operated (Transl.)

207-230°). By rehydrogenation over Catalyst No. 1930, about 25% of the distillation bottoms may be converted into monomeric 1-decyl alcohol.

The results of the i-nonylene oxation were summarized in laboratory Report No. 467/44, dated 20 July 1944.

No difficulties are involved in a plant scale oxation process. It had been planned to oxate large amounts (several tank cars) of i-nonylene in Leuna, so that, besides a greater yield of alcohols, also the necessary experience for continuous operation of the process could be gathered. Under the given circumstances, this project had to be discontinued for the time being.

Examination and Oxation of the Neutral Component from the Palatinol HS Manufacture. (*)

Dr. Jagemann gave us the neutral component from the newly installed Palatinol HS manufacturing plant, Leuna. This product was to be examined as to its use as crude product for oxo alcohols. Since our examination of this product showed that about 40% alcohols are still present, the product had to be first of all dehydrated. Since the higher boiling components of the neutral portion are to be used for special purposes (varnish solvents), special attention was given to the fraction boiling up to 130°. The fraction boiling up to 130° amounts to only 15% of the total neutral component and 75% of it may be converted into oxo alcohols.

The Preparation of i-amyl alcohol by Oxation of i-butylene.

For certain specific purposes, the i-amyl alcohol obtained from the i-butylene synthesis was found to be insufficiently pure. It is therefore desirable that a somewhat different synthesis be

(*) Palatinol HS = probably a German trade name (Transl.)

planned which yields a purer i-amyl alcohol. Since, furthermore, it seemed to be of great importance and usefulness to us to work on a larger scale with such a low boiling hydrocarbon as i-butylene, experiments in Me 458a were begun. In these experiments it was only possible to work discontinuously. In one reactor, a mash containing about 10% catalyst was placed. As mashing liquid, n-propanol was used for the first charge. For all subsequent charges, the i-amyl alcohol obtained from the synthesis was used. The i-butylene together with the cycle gas, was introduced in liquid form at the bottom of the synthesis reactor. The isobutylene was introduced very slowly, so that it could react to a great extent while in the reactor. The reaction temperature required for i-butylene lies somewhat above the critical temperature of isobutylene (reaction temperature = 155-160°; critical temperature = 150.7°).

The aldehyde formed in the primary reaction was hydrogenated further in the same reactor into alcohol. The mash was then filtered. The catalyst could be used again. In some experiments the losses were especially high, because it was not always possible to cause the i-butylene to react. In such cases, it was to a great extent carried out of the reactor and recovered in the separators, etc.

From the crude alcohol obtained after hydrogenation, a pure i-amyl alcohol may be prepared by careful distillation. A sample of 100 liters of this i-amyl alcohol was sent to I.G. at Grissheim for the manufacture of xanthogenic acid esters.

The crude oxidation product contains only approximately 50% i-amyl alcohol 3-methyl butanol-1; the rest consists of esters and acetals. The experiments for the improvement of the yield of the desired i-amyl alcohol had to be interrupted before any useful results had been achieved.

The process used in Me 458a is not recommended as plant scale process. However, a great deal of technical experience was gathered; on the basis of this experience it is to be expected that a plant scale continuous oxidation of i-butylene with the mash process will be possible. The work done on the i-butylene oxidation has been summarized and will soon be published in one of the laboratory reports.

The Determination of Small Amounts of Oxygen in Nitrogen.

For the purpose of controlling the nitrogen purified over hot iron catalyst in 458a (See assignment 813a), an oxygen determination method was developed. The oxygen content, after purification, lies below .02%, so that a determination by the Drehschmidt analysis would not be feasible. Thus, in order to get a current control of the oxygen content and in order to recognize immediately a breakthrough of the purifier, a method of determination by means of an indigo vat was worked out. Briefly, the method is based on the following principle: An indigo dye is prepared with an excess indigo and filtered through a frit (air being excluded). The yellowish dye is then led to a washing bottle through which the nitrogen to be analyzed is led. The nitrogen flowing through is measured by means of a gas meter. 0.2 cm³ O₂ are sufficient to turn the dye blue. Thus, the determination is very sensitive.

For instance, with .01% oxygen in the gas, only 2 liters of gas have to flow through the wash bottle before the dye's color turns blue. The method was calibrated by two control methods, namely the manganese-hydroxy method and a new heat gradient apparatus newly developed (Dr. Gaulrab) and installed by the plant management. The indigo dye method could be tested only for a few days preceding May 12th.

Substitution of the Catalyst Carrier Substance by Talcum.

In order to protect valves and other hard metal parts of the machinery which are hard to get, experiments were made to substitute talcum for the strongly abrasive Kieselguhr so far used as catalyst carrier. For this purpose, a small high pressure installation was built; its essential elements were: A Balcke pump, a high pressure separator, a release mechanism and a low pressure container from which the pump again takes suction. The whole apparatus was thoroughly washed with oil; it was then run for 24 hours with pure oil in order to find out whether the valves would hold when pure oil is used. An ordinary high pressure valve worked without any trouble at all, and had never to be reset during the operation.

When fine talcum was mixed with the oil, the valve had to be reset after several minutes. After at most 30 minutes, the valve had been ground to such an extent that at an injection rate of 100 liters/hour the operating level could no longer be maintained.

The experiments were carried out three times with the same results. It seems therefore that the exchange of the hard carrier substances with talcum or similar soft mineral materials for the avoiding of erosion offers no promising improvement.

The Oxation of Cyclohexene.

Experiments were begun for the preparation of hexahydro benzyl alcohol through the oxation of cyclohexene; by dehydration of the alcohol into methylene cyclohexane and repeated oxation and hydrogenation, the B-cyclohexyl-ethyl alcohol was to be prepared. This alcohol was then to be converted into cyclohexyl ethylene by splitting off of water; the cyclohexyl-ethylene was then to be examined as to its possible use as starting product for the manufacture of artificial materials by polymerization. Thereby, it is to be attempted, by use of suitable olefins and by a succession of repeated oxations and dehydrations, to arrive at certain definite classes of substances; the purpose of this being to inhibit as much as possible the bond isomerization (migration of the double bond) which occurs so easily in both the reactions.

The oxation of the cyclohexene was carried out with a rather large batch in reactor 5 in Me 458a. 150-180 liters of a mash with 4% reduced Ruhrchemie catalyst in cyclohexene was pumped into the reactor from a vessel provided with an agitator (initial vessel of the experimental plant Me 458a); through the reactor, gas was recycled in order to avoid precipitation of the catalyst. After purging three times with CO/H₂, CO/H₂ was added under a pressure of 200 atm., and after regulating the flow to 100 m³/hour, the reactor was slowly heated. At about 115-120° the reaction started and a temporary temperature raise up to 180° could not be avoided despite immediate turning off of the heater and cooling. After termination of the reaction, and cooling down to 90° (about 1 hour after the beginning of the reaction), the pressure was reduced to 10 atm.;

the reactor was then flushed three times at 50 atm. with H₂; then H₂ was again added under 220 atm. and the reactor was heated with a gas flow of 60 m³/hour.

This temperature was maintained for one hour; the hydrogenation was thus complete. After cooling down to 80° the reactor was emptied. The crude alcohol obtained after separation of the catalyst was distilled in the plant (column 13) and the pure hexahydro benzyl alcohol (of a faint --illegible*-- odor; boiling pt. = 184-185°) was obtained with a 75% yield as calculated on the crude alcohol before distillation. The first runnings, plus a small intermediate fraction, amounted to 15-20%; the residue of about 5% contained high boiling secondary products of the oxo reaction.

~~(Attached figure entitled "Gas Balance for the Continuous Oxidation of C₁₁/C₁₂ Boiling Fraction" largely illegible and not suitable for reproduction.)~~

* Could be "camphor like" (Transl.)