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THE STATE OF THE SYNOL-PROBLEM

by

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The present report is the continuation of the report of November 18, 1940, "The State of the Hydrocarbon Synthesis from CO + H₂ in Leuna." It is a compilation of the essentials in this field. Separate treatises and reports on the Hydrocarbon Synthesis exist.

STATEMENT OF THE PROBLEM

It has been recognized that the reduction of CO by H₂ at medium pressures can be directed in such a way, that besides hydrocarbons noteworthy quantities of alcohols and even high molecular portions of them can be obtained. The task therefore, arose to increase these alcohol portions. The peak values of some experiments had to be reproducible and had to be worked out to the point where they could be transferred to an operation on a large scale (see items A-C).

The formed amounts of hydrocarbons and alcohols had to be separated by usable and economical methods and the single components had to be isolated in the required purity (see items D, E).

The synol-synthesis yielded, for the first time in a primary synthesis, a reportable degree of alcohols above C₁₀ and higher molecular weights in continuous transition. We had to find an application for the alcohols which had not previously been put on the market. (see item F). However, the demand for gasoline and Diesel oil during the war is even more urgent than for alcohol. The task therefore is to find the proper conditions for the synthesis of these motor fuels and to get the blue-prints for the construction of the plants, which might be used, as far as possible, also for the synthesis of synol and could be reversed without

great costs at a later date. (see item B).

A. Conditions and Experiences in the Synol-Synthesis.

1. Carbon Monoxide Content of the Synthesis Gas.

The synol-synthesis on a fused catalyst uses CO:H_2 in the ratio 1:0.75. It is appropriate for the utmost utilization of the gas to have this ratio already in the inlet gas.

Recent investigation proved that alcohols can also be obtained with ordinary water gas, for example, $\text{CO:H}_2 \approx 1:1$ or 1:1.1. In these cases, with a higher consumption of CO percent, fresh gas may be admixed after the first stages.

2. Synthesis Pressure.

To get a high percentage of alcohols in the products, it is necessary to avoid the overheating of the catalyst. For that reason, converters with excellent heat removing qualities have to be used; for example, pipe converters with pipes of 14 mm. diameter or plate converters. (see item B 2).

It is not advisable to use a synthesis pressure above 30 atmospheres. With higher pressures, the catalyst becomes sooty, and its lifetime decreases. We also have to provide additional precautions for heat removal; for example, by cooling pipes if we choose the application of higher pressure.

Also, due to higher pressures, a shift towards an undesirable phase of product composition occurs. At 40 atmospheres, and more so at 60 atmospheres, the obtainable products were richer in high-boiling residues than at 25 atmospheres. Besides this, above 25 atmospheres, the formation of iron carbonyl increases.

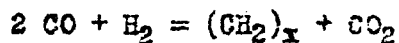
For these reasons, the conclusion that the Synol Synthesis is not planned at pressures greater than 25 atmospheres, is the most important decision in our plans for the 10,000 ton/year installation.

3. Stage Number and Synthesis Temperature

For the optimal formation of alcohol and in order to force back the Hydrocarbon Synthesis, the formation of CO₂ per synthesis stage has to be not higher than 10 percent, maximal 15 percent (measured in the residual gas in percent by volume). The less CO₂ formed, which means lower conversion work per stage, the higher is the alcohol content in the product. For practical reasons, however, we can't use too many stages. For the synol conversion, we chose four stages. For the hydrocarbon conversion, three stages are enough.

With a given CO content, gas-pressure and catalyst, we have only one degree of freedom for the regulation of the conversion left, the temperature. One employs this practically alone to fix the performance of a converter.

By determining the CO₂ content in the final gas, we have the means to detect the kind of synthesis going on in the concerned stage because the oxygen of the gas, as far as it is not built into organic compounds, is predominantly eliminated as CO₂. This is at least the case with the use of our fused catalyst WK17 under the conditions of the synol conversion,



The temperatures of the conversion in the first stage, with a methodical treatment of the fused catalyst, are about 190 - 195°. In the next stage, they have to be increased, but they should not exceed 210 - 215°.

if possible, because the alcohol content decreases distinctly, with rising temperatures.

The reason for the necessary increase in temperature is the enrichments of the gas in inert gas, mainly CO₂. This CO₂ has to be removed between the single stages in case it is increasing too fast.

4. The CO₂ Washing

An increase of CO₂ in the gas has to be avoided. It has the action of a catalyst poison, since the necessary increase of the temperature decreases the alcohol yield.

The simplest method would be to use catalysts which eliminate the oxygen of the gas only in the form of water, like the Co catalysts. However, our experiments with them show, so far, that we are indeed obtaining a noticeable increase in the alcohol content but not a decisive one.

Two processes are available for the CO₂ removal:

a. Washing by pressure water : In Me 776 we used for some time a washing tower for the removal of CO₂ with hydraulic operation. Since the installation is very small, no mass balance calculations could be carried out so far. It has been ascertained by now, that the washing out of the CO₂ between the conversion stages is in principal possible. The purification, obtainable by the indirect regeneration of the water, is sufficient for the operation of the next stage at lower temperatures.

b. Washing solutions which can be regenerated like Alkazid : In an experiment in Me 776, we try to find out whether the lye causes corrosion, foaming, or some other undesired phenomenon. One preliminary test appeared to be favorable.

In case we succeed in removing the acids formed in the conversion by condensation and at the same time to avoid a damage to the Alkacid lye, this process most likely will be superior to the hydraulic washing, since no gas and product losses occur and hot gases in the form of residual gases are available for the regeneration of the Alkacid liquor.

5. Sensitiveness of the Catalyst Against Sulfur

Since we depend in Leuna on a uniform supply of gas from a single source and additional piping can't be built on account of the war, we couldn't carry out systematic experiments. A larger H_2S content damages the Fe catalyst.

At the same time, however, it was also observed that organic sulfur compounds in the inlet gas, gave another picture. It was, for example, shown that a pretreatment of the melted catalyst WK17 with carbondisulfide after a short post-reduction, did not influence the catalyst activity so that the Synol Synthesis carried on with practically the same temperature and yields. Sulfur in organic form was continually thrown off the catalyst when sulfur poor synthesis gas, was charged over the catalyst.

We could draw the conclusion from this experiment that (under certain circumstances after a corresponding pretreatment of the catalyst) organic sulfur could be present in the gas without damaging the conversion. The primary products in this experiment with a catalyst poisoned by sulfur left the converter surprisingly much clearer than without the sulfur compounds. (Suppression of the Fe carbonyl formation?)

B. Conversion Layout

1. Auschwitz and Leuna-Sud

The blueprints for the projects Auschwitz and the Synol-plant Leuna-Sud had to be ready in the spring of 1941. It had been decided that the Auschwitz plant should produce Diesel oil and gasoline for the war effort and after conversion produce synol with a high alcohol content for peace requirements.

As a basis for the project the results of the experiments at Me 776 were available. They had been carried out for the major part with converters containing 3 liters catalyst, for the smaller part with 100 l. converters. The following guide lines, which could still be used, have been issued:

Layout for a Synol-Synthesis Plant with the Provision for a Change-Over to Diesel Oils and Gasoline Productions.

	<u>I. Gasoline</u>	<u>II. Synol Operation</u>	
Temperature	210-245°	190-225°	
Synthesis Gas	Desulfurized water gas		
Pressure	Max. 25 atms.	Max. 25 atms.	
Yield in gr./Nm ³ CO+H ₂	140 gr. liquid prod.	150 gr. liquid prod.	
Basis for the project determined in small scale experiment	14 gr. gasol	15 gr. gasol 160 gr. liquid + 15 gr. gasol	
Catalyst	Fused Fe-catalyst		
Stage number	5	4	
Catalyst load =	1:250	1:150	
Catalyst: gas volume per hour			
Catalyst performance = tons/ product/m ³ catal./day	0.92	0.60	
Catalyst lifetime	1/2 year	3/4 year	
Catalyst total performance = to prod./m ³ catalyst	168	164	
Boiling points of the liquid products:			<u>Alcohol Content</u>
Up to 200°C.	40-70%	44-60%	40%
200-300°	30-15	18-15	56
300-400°	30-15	15-10	50-60
400°		23-15	30

For the treatment of the products, the blueprints M-3675a-8 for
Muscovitz-benzene and M-4842a-1 for the synol-plant Leuna have been
supplied.

2. Construction of the Converters

The necessity to use converters with an efficient heat-removal
and with a low layer height suggested a plate-converter as an appropriate
construction. With a make-shift 100 liter pressure plate converter, syn-
thesis studies have been carried out in No 776, which proved that the
determinations made with pipe-converters can be applied also for plate-
converters.

A larger 2500 liter plate-converter will be assembled on the
Ley-square beside the pipe-converters in the summer of 1942.

In connection with the above-mentioned construction projects,
a pressure-plate converter has been built in the beginning of 1941, which
was further improved in partnership with the construction firm, Mittel-
stahl and Mannesmann. A construction plan by Mittelstahl was of great
help. It was developed by careful and detailed tests for the purposes
of the Synol-synthesis to a point where we may consider it to be the
best construction now in existence.

The following improvements have been attained: The cooling
water supply has been improved as much that the amount of the circulating
water has been quadrupled. By a slight inclination and the discharge
of the water accordingly, a safe removal of the developing steam bubbles
in the water filled pipes has been assured.

The converters have been built as twin-converters in two sizes:
 $2 \times 6m^3$ catalyst space and $2 \times 12m^3$ catalyst space.

The principle of the converters is shown in the following diagram. (Fig. 1) The plate-bundles are attached to a middle support with extensions to both sides. They are filled with the catalyst. This is done by pulling off the pressure jacket. No steam, gas or product-pipes have to be loosened in this operation. The plate bundle is within a sheet iron jacket which can be easily filled with an inert gas. The fresh gas enters uniformly from the top and passes over the catalyst. After the conversion it is carried away together with the vapor-like part of the product. The high boiling product separated as a liquid within the converter is drawn off at the deepest spot of the converter-jacket. The converter has a slight inclination, in order that the steam bubbles developed by the reaction heat can rise within the cooling pipes. The inclination angle is 6°.

The following converter units are provided for the 10,000-ton/year plant at Leuna-Sud:

10 converters with 6m³ each

1 converter with 12m³

All converters are being planned, for the time being, as single converters and will be built as twin converters in a future extension of the plant.

C. Catalytic Problems

1. Fused Catalysts

We made every effort to make this catalyst type qualified for the operation, after it had been recognized that it is able to catalyze the Hydrocarbon-Synthesis. The reasons were its solid mechanical conditions, the easy and cheap way of production in an always uniform quality, and finally the convenient way to regenerate it.

The best fused catalyst is still the Leuna ammonia catalyst

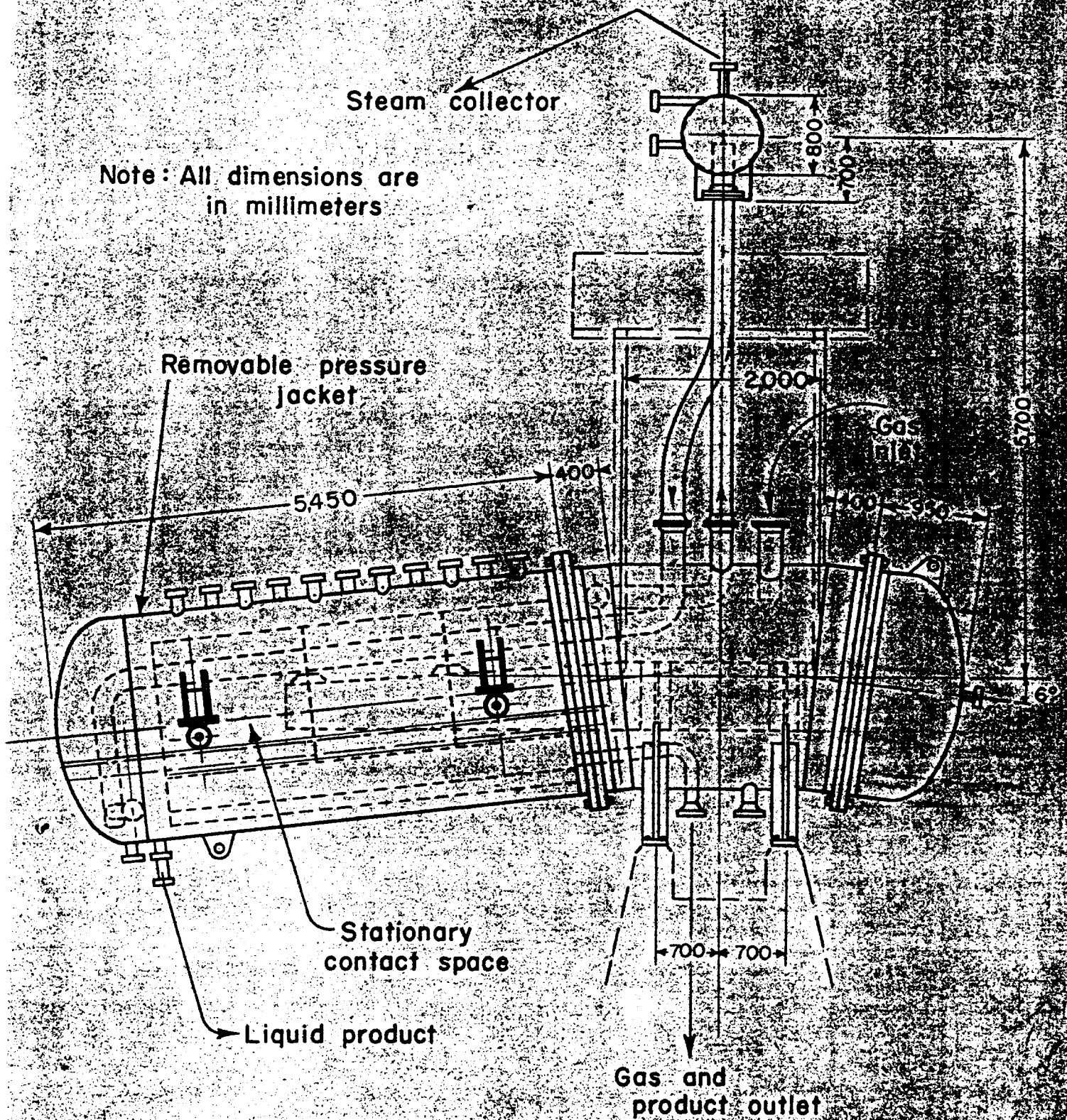


Figure 1.—

No. WK17. It will be used therefore in the converter project planned or under construction, though some of the precipitation catalyst may have some advantages.

It is being used at present in a size of 1 to 2 mm. The pour weight is 2.0.

The Oppen experiments found that WK17 during the conversion forms hexagonal iron carbide, Fe_2C , which at temperature above 290° , is transformed into inactive Haggs' Fe_2C .

a. Reduction: A reduction of the fused catalyst by a very heavy H_2 -load proved to be of the utmost importance for an efficient Synol-Synthesis, because the temperature could be kept low.

The obvious reason for this phenomenon is: the catalyst is most active, at the lowest temperature, if it was reduced as far as possible without being damaged. It is necessary for this purpose that the water steam formed during the reduction is carried away from the catalyst as fast as possible, that means, much and very dry H_2 has to be available. The catalyst will be damaged when it is heated too long and at too high a temperature, apparently by crystallization of the iron. For obtaining the most active catalysts, we need therefore, the combination of the highest hydrogen load and the shortest time possible for heating. For our catalyst with a grain size of 1:2 mm. a reduction at 450° , for 48 hours with a H_2 -load of 1:3000/h proved to be the technically and economically optimal condition. A further increase of the H_2 -load didn't have any advantage. Information about the experience acquired here in Leuna was given to the chemists and chemical engineers working on the same problem in Ludwigshagen. The catalysts of Dr. Michael could be very much improved in this manner, and by decreasing the reaction

temperature, essential progress could be achieved.

b. Reactivation of the catalyst: After the extraction of the consumed catalyst and after a treatment with hydrogen it becomes so pyrophoric that it burns in contact with air. It will not become homogeneous any more after being melted down with oxygen, because the necessary temperature is not reached. However, by a slight oxidizing (and this is also known of other catalysts) with very diluted air it can be made insensitive. It can then be handled in the air and stored for any time and then be melted down in an oxygen stream to a homogeneous mass.

c. Special melted catalysts: Some catalysts have been melted, which may have an advantage compared with WK17.

An addition of small amounts of arsenic to all catalysts gives a clearer primary product. One catalyst (3798) containing also arsenic produces a considerable amount of esters, for example, 23-25 percent in the fraction 200-300°. This is an indication for a direct synthesis of esters or acids.

The electrically second melting of the melted catalyst brought about an improvement of the ammonia synthesis. For our catalysis this precaution did not cause an improvement of the catalyst. (WK17S).

2. Precipitation-Catalysts

It is obvious that the precipitation-catalysts on account of their large inner surface and the possibility of great variations in the conditions of their origin, are very promising for the synthesis of alcohols. As a matter of fact, peak values resulted with the use of precipitation catalyst (2645), which are above the values obtainable

with fused catalysts.

The best catalyst produced so far is 2643 with 3.7 percent aluminum oxide and about 1 percent potassium oxide, the remainder Fe. It shares the disadvantage of all precipitation catalysts, that it has to be precipitated and washed with very pure water (SO_4 -free). Its application on a large scale is therefore not practical.

Good results have been attained with a precipitation-catalyst made by Dr. Schensrman-Oppau (Fi. 1249), which requires only little washing and which can be reduced on account of its Cu-content at a relatively low temperature (220°).

During the last time Fe-catalysts of a high activity have been developed at Leuna, containing small additions, as 0.1 percent Sb, Ni, etc., which probably will soon surpass the precipitation catalysts previously obtained.

5. Sensitivity Against Air

It is understandable that the reduced catalysts are extraordinarily sensitive against air. It has been found that even the very smallest traces injure the activity of the catalyst. They can, therefore, only be transferred into the reaction vessel without being damaged, by means of containers which are specially built and filled with a completely oxygen-free inert gas.

The damage done by oxygen during the transfer appears not only in a somewhat higher temperature in the beginning of the synthesis but also in a faster increase of temperature during a longer period of the synthesis and also a shortening of the catalysts lifetime.

D. Working Up of the Products

Beside the hydrocarbons and the alcohols, which have to be

produced pure, acids and their reaction products with the alcohols; esters, which are undesired at present, also result.

Other undesired products which are present only in small quantities are aldehydes and ketones. Before, therefore, the proper production of alcohols can start, the raw material has to be freed of disturbing components, which may injure the quality of the alcohols.

1. Preparation of the raw material

a. Removal of the acids by neutralization

It can be done by dissolved or solid alkali. The resulting salts have to be separated and washed.

All the acids will be esterified by the existing surplus of alcohol if the acids are not removed and the raw product is not distilled. In this way, we get losses of alcohol and the product may easily cause corrosion.

The de-acidification can be omitted if we carry out a de-esterification, as will be described below.

b. Removal of the esters

The removal of the esters is done appropriately by saponification. Treating with alkali solutions while vigorously stirring for 30 minutes at 130°C.

Alcohols are set free from the esters and the acid component is fixed as fatty acid salt. The reactive aldehydes of the product become resinous and go over to the high boiling portion. In case the esters of the raw material are not removed, they appear during the distillation into certain boiling ranges and will later form alcohols with shorter chains and acids. Whenever these fractions are worked up,

for example, by sulfurization or by melting with alkalis, acids with shorter chains will be formed which contaminate the products (adnering odor). For certain purposes the de-esterification of the products is not necessary, even undesired, for example when the synol fractions boiling up to 160° are to be worked up as varnish solvents and the alcohols have to be esterified completely, or when the same fraction has to be worked up for gasoline and has to be dehydrated at an increased temperature over earths. A removal of the esters is probably also not necessary when the product has to be used as Diesel oil. If the high boiling fractions shall be used as waxes, the esters in this wax may eventually improve its properties.

2. Product Separation

It became evident that an exact fractionation of the products is practically indispensable for all purposes. The fractionation in the ordinary laboratory columns and in a pilot plant column in Me 776 is not sufficient for these purposes. A sharp fractionation is important first of all in the case when the fractions have to be freed of alcohols by the method of the boric acid esterification.

a. Separation of the lower alcohols

The lower alcohols up to C₃ are practically only present in the water of the product. The hydrocarbon fraction contains alcohols in noticeable quantities only from C₄ on. Up to C₆ they can be removed from the hydrocarbons by washing with water, or aqueous solutions, or aqueous methanol solutions.

This extraction occurs more or less positively if we carry out a de-esterification of the product and we wash subsequently the

alkali with water.

b. Boric acid method

The alcohols which can't be extracted any more are isolated by the boric acid method. A small technical scale apparatus for a throughput of 20 kg. alcohol/day confirmed our laboratory experiments with this method. Also the practicability of the proposed recycling of the saponification water and the boric acid was confirmed. The principle of which is shown in fig. 2.

The following points are important for the application of the alcohol separation method.

- I. The alcohol will be free from neutral oil only when the initial fractions are sharply cut. Unless this is done, especially with a content of higher boiling substances, we cannot accurately separate the boric acid ester from the neutral oil and the alcohol will contain too much of neutral oil after the saponification. With a sufficiently sharp cut, a required purity of the alcohol of 95-97 percent can be attained. Still extremely difficult, in the present equipment, is the separation of the higher alcohols $>C_{15}$ from the neutral oils.
- II. The obtainable raw yield agrees extremely well with the alcohol contents determined by analysis. The residual oils are practically free of alcohol.
- III. The isolated alcohols have a somewhat lower molecular weight than they should have corresponding to the boiling range of the hydrocarbons. This is due to the displacement of the boiling point by the hydrocarbons.

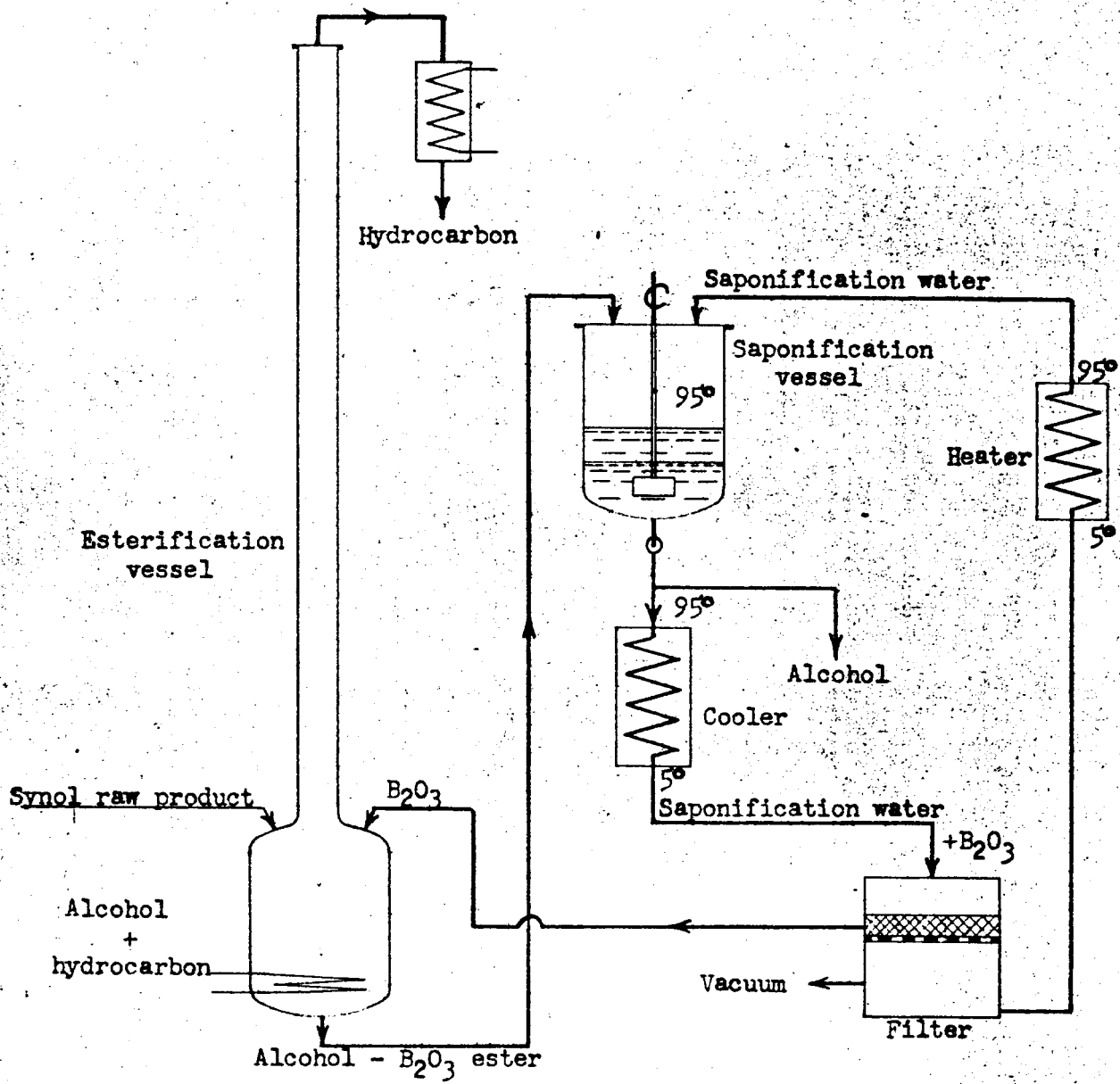


Figure 2.- Alcohol Separation. Flowsheet of Boric Acid Method.

- IV. With careful operation provided, the losses in boric acid, can be kept within narrow limits which do not encroach upon economy.
- V. For the working up of the synols, it can probably be done in 50° boiling fractions. Based on the experience with synol-alcohols, the method shall also be applied to the oxo-field. A particular advantage will be, that after the esterification of the alcohols by boric acid, we have not only the boiling interval between the neutral oil and the alcohol of a lengthened chain but this interval is pushed further up to the boiling point of boric acid ester. The possibility, therefore, exists to choose the fraction width to be set in the oxo-fraction essentially larger than this is possible by the ordinary distilling separation, probably 80-100°.
- VI. The separation of the neutral oil from the boric acid ester is satisfactory only when the neutral oil can evaporate from a thin layer, that means by rotation, by spraying, etc.

3. Distillation of higher alcohols

Laboratory tests showed, that synol alcohols can be decomposed by heating. This liability to decomposition is increased by the presence of rust and even more so by the synthesis-catalyst. The initial temperature for this decomposition of a C₁₂-alcohol is in the first case at 250°, the second case at 192°, and the third case at 190°.

It appears that we have to deal occasionally not with a simple splitting off of water, but in the presence of iron, with a dehydrogenation, that is, higher polymeric compounds are formed from alcohols. They can only be explained by an intermediate state of an aldehyde (aldehyde-polymerization). From these considerations, result the

following directions for the distillation of higher alcohols and their fractions: The temperature during the distillation within the products as well as at the walls of the still, must not go over 250° C.

The distilling should proceed quickly without unnecessary torment. Rust, catalyst dust, etc. should be kept away from the distillation as far as possible.

4. The high-boiling portions

We can isolate the alcohols from the fractions by the boric acid method as far as the accompanying neutral oils are distillable from the boric acid esters. This is the case up to about C₂₂, which has been prepared in the laboratory in a rather pure form. The fractions boiling even higher still show, for the time being, a considerable resistance to an isolation of the alcohols, We call the total fractions boiling above 400°, the "high boiling".

a. The impurities of the high boiling

The primary product leaving the converter is usually colored dark yellow. After distilling off the lower boiling fractions the coloring substances remain in the high boiling and give it a deep, dark brown color. This color obviously has two different causes:

I. Iron: The synthesis products contain, after leaving the converter, already 0.1 percent Fe. It comes obviously into the product by iron carbonyl or by dissolving of Fe from the catalyst by the formed fatty acids. In the high boiling residues, the iron is being concentrated on account of its non-volatility. It can be removed by different methods from the primary product and also from the residue. By a slight hydrogenation, the iron is obviously removed from the

product and is deposited on the catalyst. By treating the product with acids, for example, diluted HCl, the iron content can be reduced to about 1/100 of the original. The color also becomes a little lighter but can't be done away with completely. The removal of the iron from the product may become necessary if we consider the statements under D-3, in order to diminish the decomposition of the alcohols. However, a satisfactory way has not yet been found.

II. Colored Resins: As essential part of the dark coloring can be traced back obviously to resin-like components. After the first days, the product becomes darker and darker to a distinct brown, which indicates a gradual transformation of unstable substances.

III. Alkali content: By the de-acidification and the de-esterification by heat and alkali, alkali salts of the high molecular fatty acids are formed which dissolve in the hydrocarbon-fraction and are concentrated by distilling in the high boiling residue. For many purposes an alkali content does not disturb, for example, the optimal content for the oxidation of paraffin is 0.3 percent. It should not disturb the application as waxes and the like, but it has to be removed for the manufacture of candles and similar products. The greater part of the alkali can be removed by absorption.

b. Utilization of the high-boiling fractions

I. The working up of the whole product: The dark brown mass can be used for low valued products as such, for example, shoe polish, artificial wood, plates, and the like. However, in most cases a refining is desired, especially the brightening of the color. This can be accomplished by bleaching earth. We obtain by this

method light yellow products. The mass has a high softening point 70-150°, and is, on account of its alcohol content of its ester content, more ductile than hard paraffin of the Fischer-synthesis.

By a complete hydrogenation it is possible to lighten the color without residue up to colorless. The alcohols are also converted in to hydrocarbon and the product becomes very similar to the hard paraffin of the Fischer-synthesis. It is possible by a cautious reduction to get rid of the color without reducing the alcohols. This product is very valuable on account of its alcohol content, however, we do not completely control the conditions to avoid too extensive a hydrogenation.

II. Separation of single parts from the high-boiling; treatment of solvents: By treating the high-boiling with solvent, for example, by low-boiling alcohols a slight concentration of high-molecular alcohols in the solvents takes place. Moreover, we can obtain a decolorization of the high-boiling by partial precipitation of the solution.

Distillation with vacuum-steam. We can separate considerable parts (up to 80 percent) of the residue, if we treat products which cannot be separated by vacuum distillation under laboratory conditions, by vacuum-steam. The distillate is a ductile, slightly yellowish mass with about 30 percent alcohols, which can be worked to valuable wax, ointment, etc. The final residue has a dark color and has a very high softening point of 115°. By hydrogenation it can be converted to a high-grade hard-paraffin.

High-vacuum distillation. Recently we found that the

hydrocarbon can be separated much easier by a high-vacuum short-cut distillation at a low temperature than the alcohols. A fraction of 36 percent could be worked into a distillate low in alcohol and a residue containing 83 percent alcohol. We don't know yet whether this method will be an economical one.

c. Product working up difficulties due to the presence of the high boiling

- I. Neutralization: The product has a high freezing point, if it contains much high-boiling components. In this case, it has to be treated by dilute alkali at an elevated temperature, that means, 50-90°. A considerable part of the resulting soaps are being dissolved in the high-boiling fraction. Furthermore, by means of the soaps an emulsion layer between the water and the hydrocarbon is formed which is especially troublesome during the washing of the alkali.
- II. De-esterification: The same can be said for the de-esterification. It is carried out at 130° by mixing up with dilute sodium hydroxide for 30 minutes. The lye-layer separates easily from the product. However, as soon as we start to wash out the lye we get obstinate and undesired emulsion layers which retard the procedure and cause losses. The washing out by a mixture of methanol and water gives only a partial improvement. More also, alkali is dissolved in the high-boiling fraction.
- III. Distillation: The unpleasant effects are here most evident. The further the distillation proceeds the more the high-boiling residue is concentrated in the pot of the column, but the more we also have

to apply a certain overheating of the still and for a longer period to be able to distill the volatile hydrocarbons since the high-boiling has a considerable dissolving power for the lower hydrocarbons. But, for reasons mentioned under D-3, a short heating is desirable to avoid losses of alcohol.

d. Another result of the operating stages in the presence of high boiling

On account of the disadvantages described above in the presence of high-boiling the normal way of operation is appropriately changed somewhat. The flow-sheet (see fig. 3) shows the earlier method of operation and in comparison the new way of operation, which uses practically the same procedures only in another sequence. It works like this:

- I. Separation of the distillable : All distillable is being separated by a strong heating from a still. We work practically without reflux and relinquish sharp cuts.
- II. De-esterification : The distilled fractions, which have to be de-esterified are singly collected and are de-esterified together. The product can now be washed out without a noticeable formation of emulsion. The solubility of the fatty acid salts is also not so noticeable.
- III. Fractionation : The following fractional distillation is now proceeding much faster than it would in the presence of the residue and without overheating. The alcohols are less decomposed and the cuts become much sharper.
- IV. Working up of the residue : According to the intended use it can

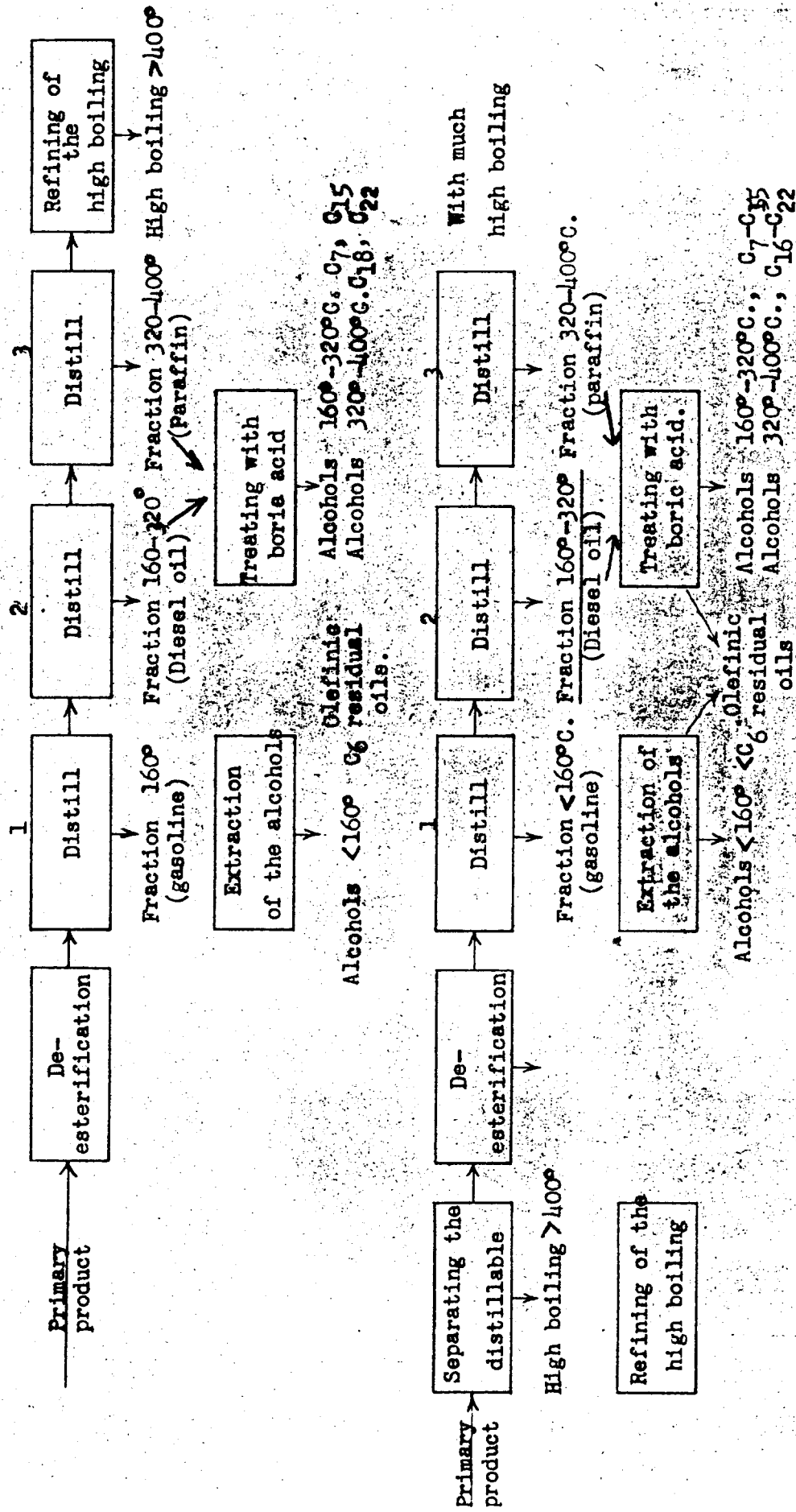


Figure 3, - Working up of the Synol Products.

be carried out by the method described under D-3.

E. State of Knowledge of the Products.

1. Constitution generally

We believe that the substances of the synol synthesis are much less branched than the alcohols of the isobutyl-synthesis. The results can't be uniformly explained yet. We have the following picture: the synthesis products have prevalently a straight chain. They contain only shorter side-chains. However, the average length of the side-chain is not so great that the prevalently straight-chain character can disappear.

Up to C₉ they are practically straight-chain and primary alcohols. Secondary alcohols can't be detected. The same is true for higher alcohols. They have a low iodine number because of incomplete purification which may be traced back to contamination by olefins. Relatively little methanol and ethanol are formed.

The double bond is prevalently at the end of the chain. This is indicated by different reasons. A C₁₂-olefin showed by an exact determination the following position of the double bond: 60 percent α -position, the remainder is distributed among the other positions, decreasing towards the middle.

It has been shown to be likely, by model experiments, that the olefins have originally the double bonds at the end, but that they partially migrate by catalytic influences, probably by iron-carbonyl toward the interior.

It follows from the constitution of the alcohols (straight chains in contrast to the α -alkyl-branched oxol-alcohols) and the

olefin double bonds at the end with fair certainty that alcohols, besides paraffins, represent the original final products of the synthesis. Obviously, the olefins are formed secondarily by splitting off water from alcohols, whereby the double bond migrates for a smaller part to the interior.

2. Existing Types of Substances

The general rule is confirmed that the olefins and alcohols in the synthesis on WK17 yields a constant percentage of about 70-80 percent of the product. There are less olefins if much alcohol is produced (60 percent and more in the synol process).

Scarcely more than 10 percent in the single fractions are present in the primary product with WK17 as catalyst. Especially much ester is obtained with a precipitation catalyst and the addition of arsenic, (catalyst 3798), up to 25 percent in the single fractions.

Both aldehydes and ketones are obviously present in the product. The lower aldehydes can be extracted by bisulfite solutions. By ester-saponification, they are partly converted into high-molecular resins and get into the high-boiling residues.

The ketones are essentially stable substances and do not interfere with any operation. They are separated with the neutral oil and do not contaminate the alcohols.

The lower ketones as acetone, are mainly found in the reaction water or reach the watery solutions during the extraction.

Other oxygen-containing compounds could not be detected, as acetals, unsaturated ethers, lactones, etc. Their total amount cannot be higher than maximal 1 percent.

E. Isolated Products

So far, alcohols from C₁ to C₂₂ have been isolated. Also isolated was acetone and acetaldehyde.

F. Application of the Products

By cooperation of numerous manufacturing plants of the I. G. an application has been found for practically all olefinic and alcoholic fractions of the synol-product. The applicability of a part of the products has already been tested.

A survey of the possible applications is shown in fig. 4. There wasn't any doubt about the quality of the alcohols and olefins for the production of washing agents. However, the applicability of the following synthesis products has to be emphasized.

The alcohols C₇-C₁₁ can be used as components of the esterification with acids of the same length of chain as the first runnings-fatty acids, or the smelting fatty acids from our alcohols, as softening agents for plastics.

The alcohol range C₉-C₁₄ can be used by Dr. Zorn as second esterification component beside isobutyl-oils. He urgently asks for synol-and oxo-alcohols in order to extend in large the production basis for these esters. Desirable would be about 3-4000 tons per year alcohols, which could be produced with synol and oxo. The production would be very important for war purposes but is also interesting in peace time.

The lower alcohols in the range from 80-200° = C₃ - C₈ could be used as ester component for varnish solvents and varnish softeners. This field is also interesting for peace time production. The advantage of this products in comparison with the corresponding alcohols from the

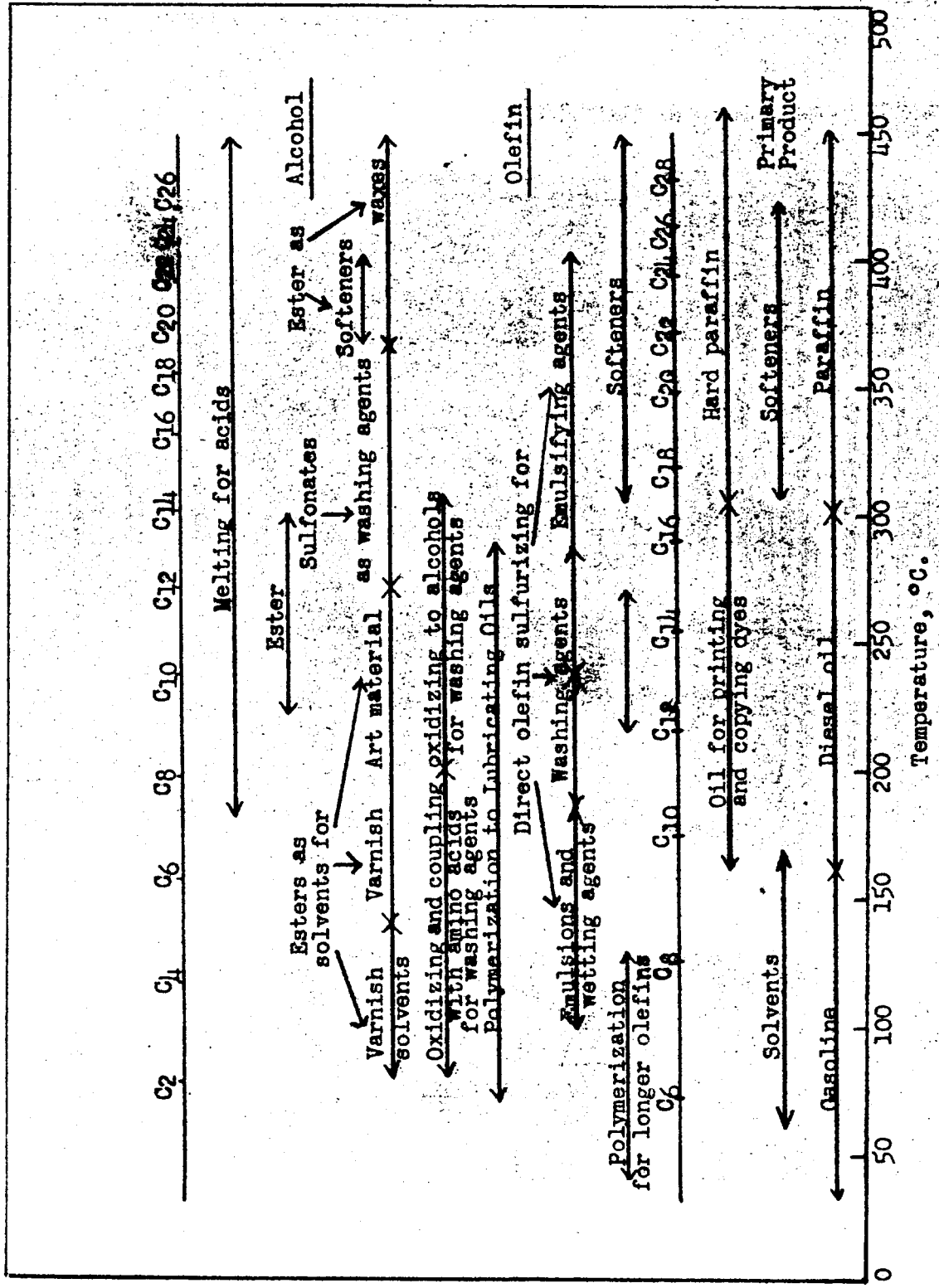


Figure 4.- Application of Synol Products.

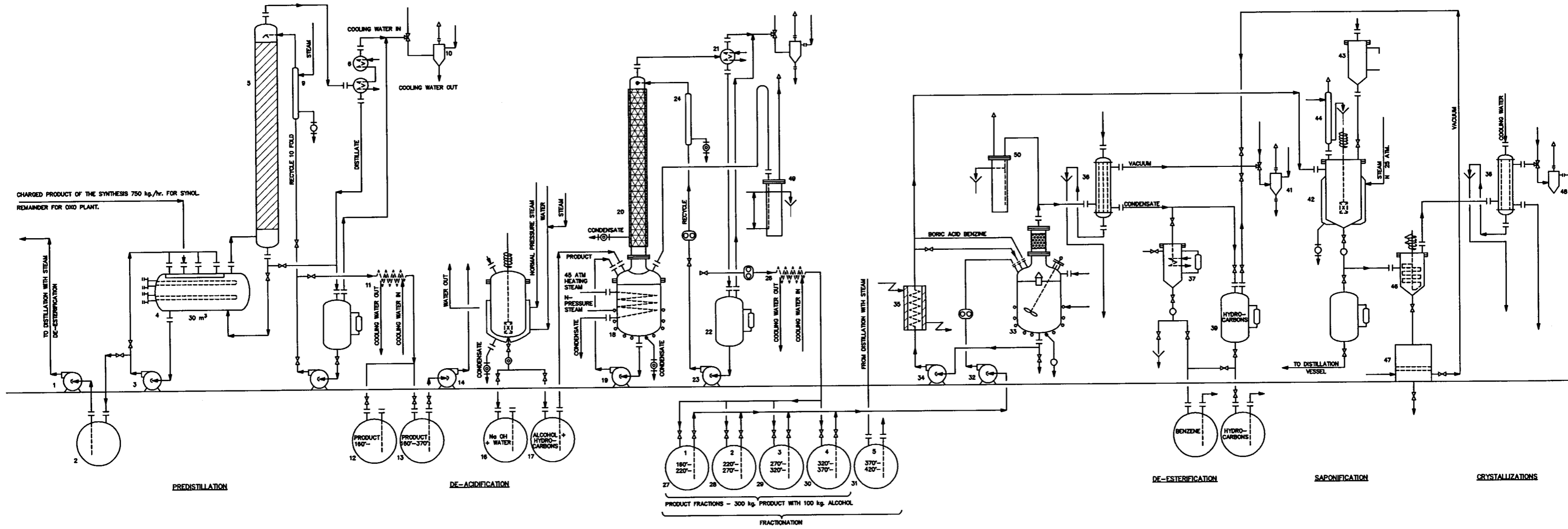


FIGURE 5 - SCHEME FOR THE WORKING UP OF THE SYNOL PRODUCTS IN ME 458.

Key the Figure 5.

1. Product Pump.
2. Vessel for Product ($>370^{\circ}\text{C}$).
3. Circulating Pump.
4. Distillation Vessel, 30 cubic meters.
5. Distillation Column, 600 mm. diameter, 10 m. high.
6. Condensars.
7. Receiver.
8. Reflux Pump.
9. Reflux Preheater.
10. Vacuum Ejector, 500 cubic meters capacity with 2 mm. Hg.
11. Cooler.
12. Product Vessel ($<160^{\circ}\text{C}$).
13. Product Vessel ($160^{\circ}-570^{\circ}\text{C}$).
14. Product Pump.
15. Pressure Vessel, 800°C . heating with normal pressure steam, cooling for 25 atmospheres.
16. Container for $\text{NaOH} + \text{H}_2\text{O}$.
17. Container for De-acidified product (alcohol and hydrocarbon material).
18. Distillation Vessel (1000 mm. diameter, 0.5 cubic meter capacity).
19. Circulating Pump, $1.5 \text{ m}^3/\text{hr}$.
20. Distillation Column, 6 meters high.
21. Vertical Condenser, 2000 mm. high. Cooling surface 1.2 square meters.
22. Receiver, 520 mm. diameter, 1000 mm. high, capacity 0.2 cubic meters.
23. Reflux Pump, $1 \text{ m}^3/\text{hr}$.
24. Reflux Preheater.
25. Steam Ejector for 2 mm. Hg., 1000 cubic meter capacity.
26. Cooler.
27. Container for Fraction I.
28. Container for Fraction II.
29. Container for Fraction III.
30. Container for Fraction IV.
31. Reserve Container.
32. Product Pump.
33. Vessel for Esterification, 600 mm. diameter, 450 liters capacity.
34. Circulating Pump.
35. Electrical Preheater.
36. Vertical Condenser, 133 mm. diameter, 2000 mm. high, cooling surface, 21.2 cubic meters.
37. Separator, 267 mm. diameter, 1000 mm. high capacity 0.2 cubic meters.
38. Vessel for benzene.
39. Receiver, 520 mm. diameter, 1000 mm. high capacity 0.2 cubic meters.
40. Vessel for hydrocarbon material.
41. Small Ejector.
42. Saponification Vessel, 600 mm. diameter, 200 liters capacity.
43. Measuring Vessel.
44. Reflux Cooler.
45. Receiver, 520 mm. diameter, 1000 mm. high, capacity 3.2 cubic meters.
46. Crystallization Vessel, 800 mm diameter.
47. Boric Acid Filter, 800 mm. diameter by 1500 mm. capacity 200 liters.
48. Steam Ejector for vacuum.
49. Safety Quench for No. 20.
50. Safety Quench for No. 33.

isobutyl oil synthesis is said to be the better odor of the straight chain substances.

The synol fractions up to about 160° after the esterification of the alcohols by acetic acid have a limited interest as direct solvents.

According to earlier experiments, a standard gasoline with good resistance to knocking can be produced by the gasoline and also by the synol-process, (octane number 66, if only de-esterified, 72, if treated catalytically by earths). The Diesel oil can be out within the boiling limits 160 to about 330°, and is unobjectionable and complies with standard requirements.

G. State of the Equipment

1. 10,000 ton/year plant at Leuna-Süd

Projected and applied for is a plant which shall produce gasoline and Diesel oil during the war. Concerning the lay out plans, see B-1. The orders for the long-time apparatus were issued largely in 1941, but were cancelled in October 1941. They shall be sent out again, since the government has recently recommended the construction of the plant.

2. Pilot plant 458

At this time, a pilot plant is being finished and is just starting operation at the Ley-square, which is supposed to produce olefins for the operation of an adjacent exo-plant No 458a. It is characterized by the following details:

1. Reduction of the catalyst: Available filling space (with 1400 mm. inner width and with 320 mm. pouring height) 500 liters, amount of recycle- H_2 per hour is equal to 1000 m^3 . H_2 -load = 1:2000/.

- II. Converter Plant: Four pipe-converters, 750 liters catalyst space each, 4.5 m pouring height, two of the converters have 1400 pipes with 15 mm. inner width each and two converters have 709 pipes with 20 mm. inner width each. In spring the first plate-converters built for synol with 2.6 m^3 catalyst space, 1.60 m pouring height, and 7.5 mm. distance between the plates shall be set up.
- III. CO₂ - Washing: Washing towers 450 and 400 mm. inner width, available washing space $2.5 \text{ m}^3 / 2.0 \text{ m}^3$ with 16 m. pouring height.
Filling bodies 50 mm.
Maximal water circulation $\dot{V}_h = 50 \text{ m}^3$.
- IV. Tank Depot: 10 vessels with 10 m^3 available filling space each.
- V. Distillation: Still with 30 m^3 useful space, reflux output of the still pump, $120 \text{ m}^3/\text{h}$ heating surface of the still heating $20 \times 14 \text{ m}^2$ packing bodies ~ 30 mm. (folding bodies type 4). Highest possible vacuum by a Wiegand steam jet ejector 10 mm. Hg.
- VI. Active Charcoal:
A-Cool: Four towers 3 m^3 each reversible. Planned absorption time until reversion for regeneration: 30 minutes.

3. Manufacturing plant

Samples in large numbers have to be produced as soon as possible to create a demand for the synol products according to the mentioned different application purposes. This work is beyond capacity of the laboratory.

A small manufacturing plant has, therefore, to be built at the Ley-square. The synol converter of this plant has to be operated in such a way that the product has the characteristic properties of synol, (low layer height, low load of gas). The projected plant is shown in fig. 5.

4. Pilot plant experiments in Me 776.

Available are pipe converters 14 mm. diameter

1 Converter	95	liters	4	m. height of layer
2 Converters	81	"	4	m. "
1 Converter	36	"	4.4	m. "
1 Converter	16.8	"	4	m. "
1 Converter	12	"	1.5	m. "
2 Converters	10.9	"	4	m. "
1 Converter	4.8	"	1	m. "
1 Converter-high pressure	3	"	1	m. "
6 Converters	3	"	1	m. "
1 Converter, catalyst around the pipes, 17 liters, 1m. height of layer.				
1 Plate Converter with about 150 l. catalyst space, 12 mm. plate distance, 0.7 m. height of layer.				
1 pressure water washing with 150 l. washing space.				
1 Distilling column, 300 l. still content for atmospheric pressure.				
1 De-esterification vessel, 150 l. content were run especially in Me 776. The catalysts which had operational tests proved well in the laboratory converters were tested extensively.				

5. Laboratory experiments - Me 245.

Catalyst experiments are carried out in nine 200 cm³ 1-pipe converters at 25 atms. Other experiments are taking place on the working up of products and improvements, isolation of alcohol, determination of the constitution etc.

H. Operational Program

Conditions of war impose so many restrictions upon us, as far as co-workers, specialists, materials, etc. are concerned that our plans can be only extended to the most important work. We are, on the other hand, compelled by the necessities of war to direct our work to a production which we will have to abandon after the end of the war. We have to decide, therefore, between an immediate object, in which we accommodate ourselves to present conditions, and a distant object for peace conditions, for which we can work only conditionally.

Immediate object

After a successful start of the pilot plant at Ley-Square,

the working up of the products shall begin as soon as possible. We try to obtain about 100 kg alcohols daily. We want to get operational experience as well as material for working larger samples. We would like to find an application of the alcohols which does not require a separation of the neutral oil. This can be done by esterification, (ester oils), or by alkali fusion by which sodium salts of fatty acids are obtained. The high boiling residue, which still contains considerable amounts of alcohols shall also be investigated, to produce out of them, substances with high alcohol content, which may be valuable for the manufacturing of waxes and ointments.

Distant object

Further improvement of the process, for example, the increase of the alcohol content, the choice of certain fractions, a higher gas yield, the application of catalysts and conditions which form H_2O instead of CO_2 , the use of gases which are desulfurized to only a small extent. Steering the synthesis into another direction, for example, for the immediate production of larger amounts of esters and acids.

Working of the products

Methods have to be found to convert alcohols and olefins not useful in certain industries into other fields for example, by polymerization, condensation, etc. (washing agents).

We are the first industrial producers of higher straight-chain alcohols in continuous transition. The working-up methods shall therefore be secured for the I. G.

J. Various matters

1. About organization

Dr. Wintzer and Dr. Reisinger continued to work for synol. Dr. Reisinger is busy with matter of composition, production, separation and, above all, with the isolation of alcohol by boric acid, as well in the laboratory as in the pilot plant. Dr. Wintzer took care of pilot plant No. 776; being assisted from July 15, 1940 on by Dr. Breywisch.

At present, Dr. Wintzer is supervising the start of operation at the Ley-Square. From April 1 to December 1, 1941, Dr. Peinze worked on catalysts for the synol-synthesis. From this day until February 14, Dr. Pobloth carried out this work and to transfer it. After he separated with this group of workers, and joined Dr. Breywisch. During the period from September 15 to December 1, 1941, Dr. Pobloth assisted Dr. Reisinger in work on product problems.

Most of the catalysts were produced by Dr. Hula, a part of the fused catalysts by Dr. Sundhoff, ammonia-plant.

Dr. Elbel and Dr. Maunthner continued to take care of the engineering problems.

Dr. Wirth of the organic department was responsible for the designing and the construction of the 10,000 ton/year plant at Leune-Sud, he also participated in the construction of the converter (see B-2) together with the first engineer Keinke, first engineer, Dr. Sachmann, dipl. eng. von Lom, Dr. Mauthner, Schwale and Bauder.

We should mention also the cooperation of other offices in the solution of partial problems. Dr. Kaufman and co-workers (Dr. Hartmann, Dr. Wols, Dr. Hilberath) worked on manufacturing gasoline and Diesel oil from our products, Dr. Smeokal, Dr. Asinger, Dr. Richter

on washing agents. Dr. Berg carried out some experiments on the transformation of alcohols into acids, he also worked on constitutional questions. Dr. Gemassmer did work on oxidation of synol-olefins, Dr. Zorn and Dr. Metzger tested our alcohols as components of our ester oils. Dr. Lowenberg and (Miss) Dr. Kossig did research on the constitution of our alcohols, Dr. Asinger of our olefins. Dr. Heidinger tested synol as a solvent.

2. Outline of patent application

On account of the many publications the applications for the synol synthesis proved to be difficult. However, we tried to obtain an extensive protection. So far, we sent out the following applications. A part of these applications are kept "secret".

List of Patent Applications

<u>O.Z.</u>	<u>Date</u>	<u>File No.</u>	<u>Content</u>
11 999	2-8-40	I 66 476	Cooling of the reaction space by injection of overheated product (instantaneous vaporization)
12 882	2-21-41	I 66 936	Extraction of the products by methanol, etc. for the improvement of the operation.
12 858	3-19-41	I 69 189	De-acidification of the product by solid alkali before heating.
12 930	3-2-41	I 70 151	Reduction of the catalyst by flooding with hydrogen.
12 938	3-6-41	I 70 180	Improvement of the products by treating them with alkali in the heat (ester-saponification).
12 948	3-19-41	I 70 282	Recycling the product over the catalyst during the conversion.

List of Patent Applications (cont'd.)

O. Z.	Date	File No.	Content
12 963	8-29-41	I 70 367	Cooling of the final gases by direct cooling with the synthesis product.
12 964	8-29-41	I 70 366	Seating of the inlet gas in front of the catalyst space by heat exchange with the exit gas.
12 895	7-1-41	I 70 064	Isolation of alcohols by boric acid esterification by recycling the boric acid and the saponification water.
12 989	9-15-41	I 70 455	CO ₂ -washing by pressure water between the stages, which is regenerated exclusively by releasing the pressure.
13 005	9-23-41	I 70 488	Conversion in several stages by not more than 15 percent CO ₂ formation per stage.
13 010	9-24-41	I 70 503	Collective application: Low synthesis temperature with Fe-catalysts, which have been reduced by much H ₂ , and by working in several stages.
13 281	3-2-42	I 71 725	Conversion limit per stage referred to the evolution of heat.
13 345 13 346			Operation in heat-conducting converters and without additional liquid wetting below 30 atms. and with additional liquid wetting at higher pressures.

New application 492 141 addition to O. Z. 12 892 of Luana, 8-25-41. Content: Extraction of the products by water and salt solutions.

Appendix: For the synthesis of hard paraffins 12 177, 5-30-40, I 67 099 Cocult catalyst on Al₂O₃, which was heated previously to at least 850°.

With reference to "foreign applications", it has been stipulated that during the war no synol-applications shall be published.

The applications shall be confined to Germany and shall not be published. We assume that after the war we can apply for patents within the European foreign countries with a German priority and we will then take full advantage of it.

3. About Contracts

The methods developed by us do not collide in all the important parts with the rights of others for both the gasoline and the synol process. It touches only in a single point on applications of Ruhrchemie. In the middle of 1941, when large gasoline projects had to be realized, a clarifying discussion within the I. G. took place and by the contract between the law department of Ludwigshafen and Ruhrchemie, it was decided upon an agreement of purposes. Contract outlines were formulated and discussed, while Leuna participated in the elaboration. Reports and other documents had to be deposited, since the agreement had to be strictly limited to the hydrocarbon field. We wanted to emphasize in opposition to Ruhrchemie, that we had already worked out all details of the synol synthesis previous to the conclusion of the agreement and that we had recognized their importance.

We designed corresponding outlines. Both parties desisted from pursuing the matter since a special project which caused the conclusion of the contract was suppressed.

4. Additional

a. Hard Paraffin: We had worked out a hard-paraffin synthesis previous to the synol-synthesis. Using a special cobalt catalyst (Co-Zn O, on calcined aluminum oxide) we obtained up to 70 percent hard-paraffin with a very high softening point (90°) and a good gas yield. A reproduction of the catalyst for small scale experiments was possible. Sources of disturbances were uncovered and removed. With regard to the

essentially greater interest of the synol problems, we stopped working on the hard-paraffin synthesis. However, this field can claim actual interest for two reasons.

People at Wolfen are still convinced that they can produce threads and foils from high molecular paraffins. However, the samples of paraffin sent to Wolfen with softening points up to about 120°, were not satisfactory to Wolfen. Recently, we have again been contacted to attempt an isolation of the highest molecular paraffins for these purposes. On account of the labor shortage, this work has to be postponed.

People at Oppau try hard to separate the paraffin from the Fischer-synthesis, which is being worked up over there to emulsifying substances by oxidation.

All Fischer synthesis plants, one after the other, are starting the production of such emulsifying agents.

It is planned, therefore, if it is possible by any means, to build within the I. G., our own plant for the production of hard paraffin. In this case our method will be of the greatest interest, and the combination of such a plant with the synol plant at Leuna Sud would be advisable.