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The Examination of Olefinic Carbon Monoxide Hydrogenation Products
and Their Possible Application to the Oxo Synthesis, with Special
Regard to the Field of Detergents

Table of Contents

	<u>Page</u>
<u>Introduction</u>	1
The Oxation	2
Separation of the Alcohols, Sulfonation	3
Methods of Determination for the Study of the Composition of the Synthesis Products	4
Evaluation of the Analytical Results	5
Range of the Oxo Detergents and of the Primary Detergents	6
<u>Experimental Part</u>	
<u>Primary Olefin of the Ruhrchemie Inc.</u>	6
Conditions for Preparation	6
Analytical Examination	7
Composition of the Detergent Alcohols After Oxation of the Primary Olefin	7
Oxation of the Primary Olefin, Convertibility	10
<u>Carbon Monoxide-Hydrogen Synthesis Product, Leuna</u>	10
Conditions for Preparation, Analytical Exami- nation	13
Composition of the Detergent Alcohols After Oxation	13
<u>Synol Recycle Process Product, Leuna</u>	16
Conditions for Preparation	16
Analytical Examination	18
Composition of the Alcohols After Oxation	18
Oxation of the Synol Recycle Process Product	22
<u>Michael Products, Ludwigshafen</u>	27
Conditions for Preparation	27

Table of Contents (Cont'd.)

	<u>Page</u>
Analytical Examination	27
Composition of the Alcohols After Oxation; Oxability	30
<u>Lurgi Synthesis Product (Dr. Herbert)</u>	
Conditions for Preparation	30
Analytical Examination	32
<u>Cracked Olefin of the Ruhrchemie</u>	32
Analytical Examination, Oxability	32
<u>Comments on the Results</u>	37
<u>Summary</u>	42

Introduction

Within the scope of the experiments for the use of olefins of widely different origin in the oxo synthesis, olefinic carbon monoxide hydrogenation products, as obtained by different processes, were examined and subjected to the oxo reaction; their convertibility was studied. These studies were to provide us a qualitative and quantitative picture of the composition of the products obtained by the various syntheses, and an overall view as to the products most suitable for the preparation of alcohols by oxidation was to be gained. In all the products available for study, only the liquid reaction product was considered. The gaseous synthesis products such as methane and gasol, as well as the products dissolved in the product water (lower alcohols) were not further examined.

The values found, and especially the values calculated by further computation, were not rounded off on purpose, so that maximum accuracy could be achieved for the study of the overall picture. We know well that by varying the experimental conditions, such as the CO:H_2 ratio, the gas velocity, etc., the products of a synthesis may be changed. These changes however do not exceed a certain limit, i.e., they change the boiling range to a negligible extent, while at the same time showing their effect in the ratio paraffin:olefin:alcohol.

The present report is to give a cross section of the situation as it stands today, and is a contribution to any further research which might be done in this field.

Oxation

The oxation was carried out in all cases with a slurry of Fischer synthesis catalyst (Co content = about 30%) which had been previously reduced outside the conversion vessel. The oxation proper occurred at temperatures between 130 and 160°C. and at water gas pressures exceeding 200 atm., either in the autoclave or also, in part, on a semi plant scale as continuous process. After completion of the oxation the sludge was treated at 180° and 200 atm. pressure with hydrogen. Both the oxation and the hydrogenation went smoothly.

During the oxation, besides the desired alcohols enriched by one C-atom, other higher boiling products are also formed; their amount is about 10% as based on the alcohols formed. Since these high boiling products (dimeric alcohols etc.) can be sulfonated to about 2/3, thus giving valuable detergents when mixed with other alcohol sulfates, the sulfonable component of this high boiling product was calculated as detergent alcohol and considered as such in the graphical representations. Through the oxation, a weight increase of about 15% average occurs in the preparation of detergent alcohols (the weight increase is based on the amount of converted olefin). But since the oxation does not entirely reach completion (conversion being about 95-96%) and since a portion of the high boiling component is not sulfonable, only a 10% weight increase was assumed, as based on the analytically determined olefin content. The weight increase is due to the addition of carbon monoxide and hydrogen (methylol residue and hydrogen). If the above considerations are taken into account and the alcohol (primary*

*i.e., originally present (Transl.)

alcohol) formed during the carbon monoxide hydration is determined, it is possible to give a reliable evaluation of the quantitative ratio of primary alcohol to oxo alcohol. For the detergent alcohols, this may be gathered from the graphical representations attached to this report. The ratio oxo alcohol : primary alcohol also enables one to reach certain conclusions as to the properties of the alcohol sulfates.

Separation of the Alcohols

The alcohols formed during the carbon monoxide hydrogenation (primary alcohols) cannot be separated by distillation. On the other hand, a distillative separation of the alcohols formed by oxation would be possible if sufficiently narrow fractions were used as initial products. Since the purpose of the present study was to gather all those alcohols which are of interest for the study of detergents (primary alcohols and oxo alcohols), chemical and/or physical separation methods had to be used. The common separation of the primary alcohols formed during the carbon monoxide hydrogenation and of the alcohols formed during the oxo synthesis was carried out by the distillative removal of the non-alcoholic components from the oxo-conversion product and esterification of the alcohols by means of boric acid. The separation of the alcohols is also possible by the silica gel adsorption process developed by Leuna on a laboratory scale.

In our case it was found to be of advantage if the alcohol containing products were sulfonated directly; thus the entire alcohol content is converted into alcohol sulfates and the neutral oil is separated. The sulfonation was carried out between 10-30°C

with a 10-20% excess chlorosulfonic acid; the operation went very smoothly. The neutral oil was removed by extraction of the neutralized sulfonation product in aqueous/methanol solution with benzene. In this process, also the major part of the high boiling secondary products (dimeric alcohols) which are formed during the oxo synthesis, are converted into alcohol sulfates.

Methods of Determination Used

In order to determine the composition of the products to be examined, it is necessary that they be broken down into several sharply defined fractions. The magnitude of the individual fractions gives an accurate overall picture of the boiling fraction, i.e. of the distribution of the C numbers. To the individual sharply defined fractions, theoretical characteristic values for 100% alcohols, olefins and esters may now be assigned because of their boiling boundaries. By determination of the corresponding characteristic values, the exact content of olefins, alcohols, esters, etc., may now be given. One factor was neglected here: by azeotropic entraining, a small shift may occur. In the paragraphs which follow the method of distillation and the tests for the determination of the characteristic values are briefly discussed.

Distillation

Was made in a one meter long glass column packed with Raschig rings at atmospheric pressure or in vacuo; reflux = about 1:10. Four liters were distilled each time.

Determination of the Olefins

The olefin content was always determined by several different methods. Besides the iodine number as determined according

to Hanus, Kaufmann and Winkler, the adsorbed component in phosphorus pentoxide-sulfuric acid (SPL) was determined according to Kattwinkel; however, with this method all other oxygenated compounds besides the olefins are determined.

Oxygenated Compounds

The determination of the esters, acids, alcohols and aldehydes was carried out along the lines laid down in the I.G. analytical method. The alcohol content was also determined partly by sulfonation with chlorosulfonic acid.

Compilation and Evaluation of the Analytical Data

The results of the various analyses of the products examined are given in tabular and graphical form in the following pages. In the numerical tables the following data are given: the individual fractions, their quantitative amounts, the densities and the C numbers determined on the basis of the boiling ranges of the individual classes of compounds; also, the corresponding theoretical characteristic values for 100% of the class of the compound, and also the characteristic value found and the percentage computed from it. The summation of the olefins plus the oxygenated compounds should be equal, theoretically, to the portion soluble in phosphorus pentoxide-sulfuric acid (SPL). The difference between the SPL and the sum of the olefins + the oxygenated compounds (as identified by the characteristic values), should therefore = 0. As may be seen in the numerical tables, certain deviations occur in the lower boiling fractions. But in the fractions which are of importance in the field of detergents, the deviations from 0 are not very great, so that in this range especially reliable basic

values for the determination of the oxability are obtained.

From the C numbers of the olefins it can be seen that, for the detergent group, the components beginning with 175-180° (i.e. C₁₁) can be used for the oxo reaction: The entire component above 175° will henceforth be referred to as oxo detergent range. In this connection, still another concept was introduced, namely the primary detergent range. This is the range which contains the primary alcohols originally present and belonging to the detergent field, from C₁₂ on, i.e. from 225-260°.

The results tabulated in numerical form in the tables are visualized in the corresponding graphical representations. In these, the abscissa shows the content of the classes of compounds (compositions) in %; on the ordinate, the weight percentages of the various fractions are marked. The area of the entire graph corresponds to the entire amount of product. The areas of the individual classes of compounds correspond exactly to the amount of the particular class as compared to the total amount of product.

Experimental Part

Primary Olefin of the Ruhrchemie Inc.

The examination of this product and its convertibility in the oxo synthesis is of greatest significance in view of its later use in the oxo plant in Holten.

Method of Preparation

This primary olefin was prepared over Fischer cobalt catalyst at medium pressure (8-12 atm) at 180-190° from carbon monoxide

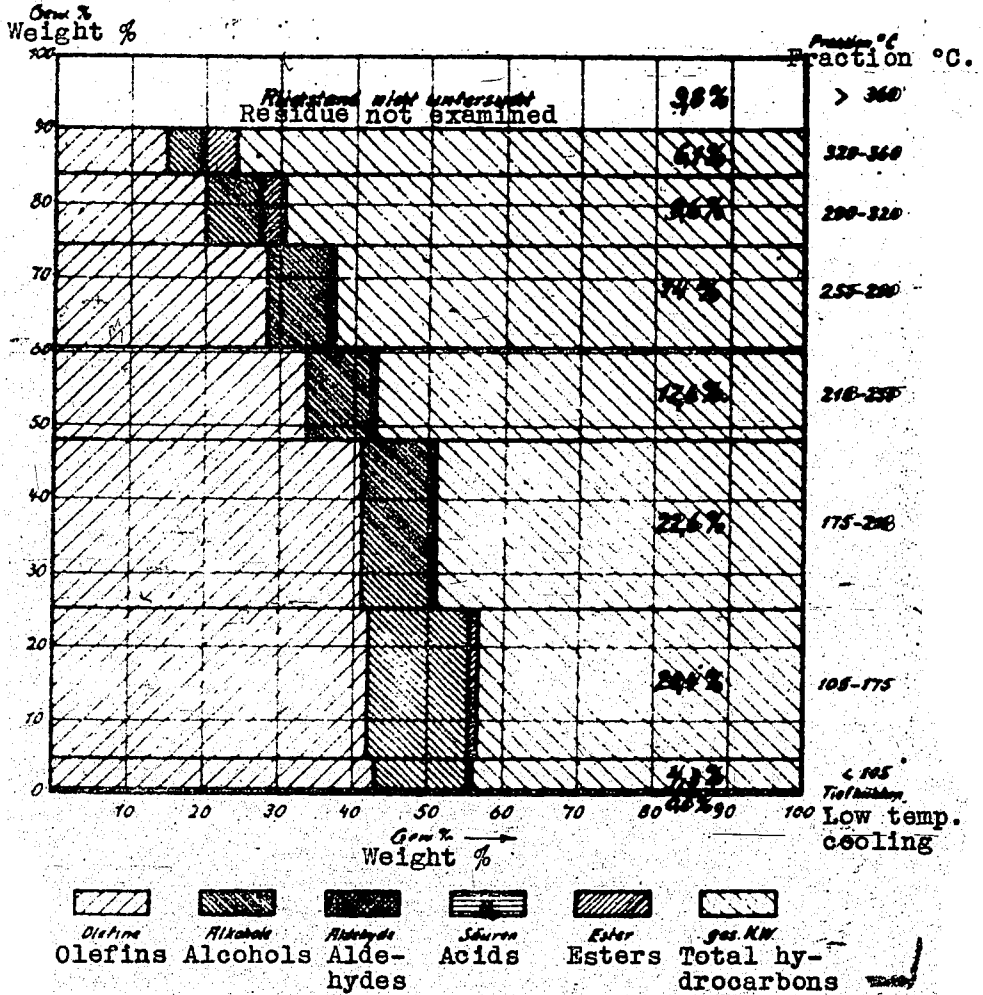
and hydrogen. The gas is converted with recycling and, contrary to the normal Fischer synthesis, the ratio of carbon monoxide to hydrogen in the cycle gas is maintained at about 1:1. Due to the high gas velocity through the catalyst and the changed CO/H₂ ratio, the olefin yield is almost tripled by the repression of hydration.

Analytical Examination

The results of the analytical examination are contained in Table 1. The alcohol content of the low boiling fractions lies around 12-13% and falls off for the highest boiling components to about 5%. Aldehydes and acids are not present, or, if present, only in small quantities. Esters too are absent in the low boiling fractions, whereas the higher boiling components have small ester contents. The olefin content decreases with increasing C number, from 43% to about 15%. The fraction with C₁₇/C₁₈ still contains 20% olefins. The quantitative distribution of the individual fractions and their composition can be more easily seen from Figure 1. Up to 175°, about 25% distill; the residue above 360° amounts to 10%. The component which may be used for the oxation in the detergent group (175-360° = "oxo detergent range") amounts to 65%, with an average olefin content of 31%. The olefin component (C₁₁-C₂₁) which may be used in the detergent group through oxation, amounts to 20% of the total product. The oxation of the wide boiling range (175-360°) produces an alcohol mixture which, when directly sulfonated, also converts the lower alcohols, which are contained as primary products in the fractions 175-218° and 218-255° (C₇-C₁₁), into alcohol sulfates. The amount of these short chain alcohols (C₇-C₁₁) is about 11.7% of the total alcohol (i.e. alcohols con-

Primärolefin der Ruhrchemie
 PRIMARY OLEFIN OF THE RUHRCHEMIE

Bild 1 zu Tafel 1
 Fig. 1 for Table 1



1705

tained as primary original product and alcohols formed by the oxo synthesis). Here, the fact was taken into account that through the oxation an average weight increase of about 10% takes place. The composition of the alcohols can be determined from the analytical results if the above observations are taken into account; the carbon distribution of these alcohols is represented in graphical form in Figure 2. In this graph, the primary alcohol content (i.e. the alcohol formed by CO hydrogenation) and the oxo alcohol content are marked on the x-axis; on the y-axis, the amounts of alcohol as based on the C number is represented. Mostly, 2 C numbers are combined, corresponding to the data in Table 1. The alcohol mixture C_{12/13} consists of about 90% oxo alcohol and 10% primary alcohol. The alcohol mixture C_{14/15} contains about 13% primary alcohol; the mixtures C_{16/17} and C_{18/19} contain about 4-4.5% primary alcohols. The alcohols above C₁₉ are exclusively oxo alcohols. In this connection it should be pointed out that oxo alcohols with such elevated C numbers give considerably more soluble alcohol sulfates (due to their branching) than the corresponding straight chain alcohols; they are therefore suitable for the preparation of excellent washing agents.

The convertibility of the olefins in the oxo reaction was determined by using, as initial product, the individual fractions of the primary olefins in the oxo synthesis. The results are tabulated in Table 2.

Hydrocarbon Synthesis Product (Leuna)

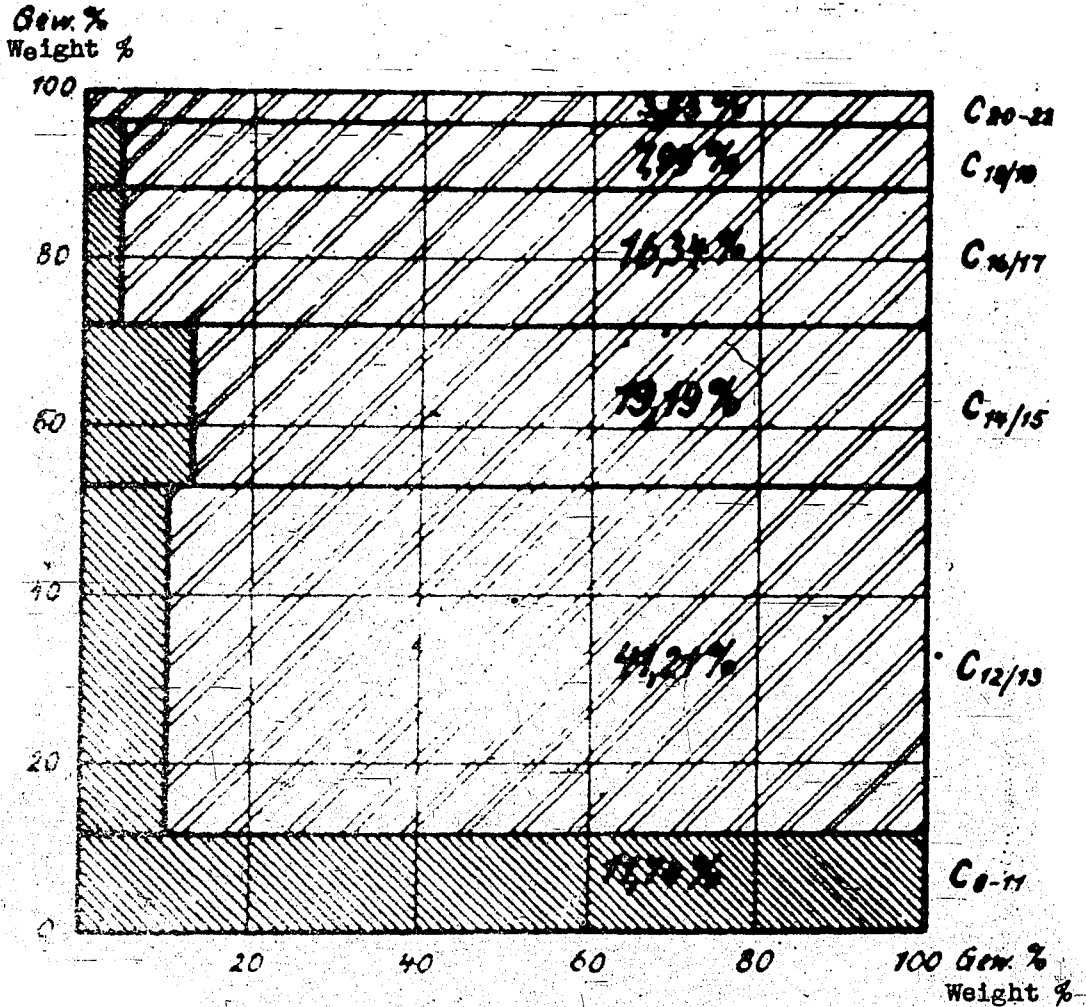
The product was prepared by conversion of carbon monoxide and hydrogen over iron catalyst in a tubular reactor. Synthesis


Zusammensetzung der Gesamtalkohole
nach Oxidation des breiten Bandes 175-360°C (Benzolmittellinie)
von Primärolefin der Ruhrchemie

COMPOSITION OF THE TOTAL ALCOHOLS
 after oxidation of the wide boiling fraction 175-360° (oxo
 detergent range) from Ruhrchemie primary olefin

Bild 2

Fig. 2




 Primäralkohol
 Primary Alcohols



 Oxoalkohole
 Oxo Alcohols

Table 2

Comprehensive Summary of the Oxidability of Ruhrchemie Primary Olefin

Fraction	Density at 20°C.	Before Oxidation				OH-No. Before Oxidation	Density at 20°C.	C-No. of the Oxo Alcohols	Theor. OH No. for 100% Alcohol	Theor. OH No. for 100% Conversion Calculated on Iodine No.	OH No. Found After Oxidation	Difference OH No. Before Oxidation - OH No. After Oxidation	% Conversion
		Theoretical Iodine No.	Iodine No. Found	% Olefin	OH-No.								
50-150°	0.718		227	97.5	77	0.787	7/8/9/10	390	167.5	240	163	97.6	
150-175°	0.743	181	81	44.8	55.5	0.790	11	326	146	200	144.5	99	
175-217°	0.750	158	66.5	42.1	37	0.790	12/13	290	122	150	113	92.6	
217-256°	0.767	139.5	45.5	33.8	35.5	0.788	14/15	254	86	117.3	81.8	94	
256-292°	0.781	117	34.5	29.5	36	0.792	16/17	224.5	66.2	100.2	64.2	97	
292-310°	0.788	105	27	25.7	21	0.797	18/19	206	53	73.2	52.2	98.5	
310-332°	0.789	97.5	22	22.6	11.5	solid	19/20	192	43.3	53.3	41.8	96.5	

The values for the conversion are average values which were obtained in autoclave experiments with greater initial amounts. In the computation of the conversion, the primary alcohol must be taken into account. This appears also from the above Table 2. The conversion, calculated from the OH No., amounts to 95-96% average.

$$\% \text{ Conversion} = \frac{\text{OH No. after oxidation} - \text{OH No. before oxidation}}{\text{Theor. OH No. for 100\% conversion calculated from olefins}} \times 100$$

temperature = 270°; pressure = 19 atm.; gas throughput calculated on the basis of the catalyst volume = 1:300.

Analytical Examination

Only the components boiling between 180 and 340° were used for examination. The components below 180 and above 340° were only collected quantitatively. The values obtained are given in Table 3 and its corresponding Figure 3.

Table 3, see p. 14.

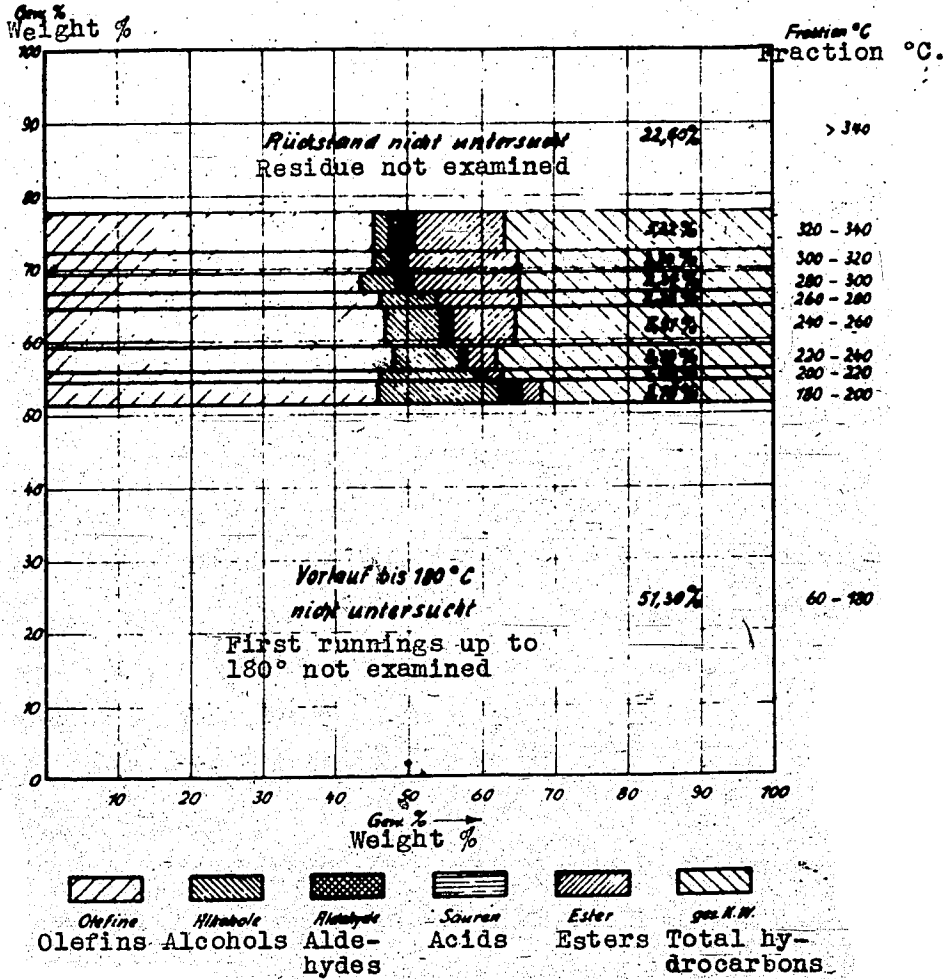
The alcohol content decreases with increasing molecular weight: in the fraction 180-200, it is 16.5%, whereas in the fraction 320-340, it is only 2.2%. Acids are present only in small amounts. However, in contrast to the Ruhrchemie primary olefin, aldehydes are present in average amounts of 1-2%, and furthermore considerably higher amounts of esters are present; the latter increase to as high as 15% in the higher boiling fractions. The olefin content too is higher and lies, in contrast to the primary olefin, rather constantly in all fractions between 45-48%.

Figure 3, see p. 15.

In contrast to the primary olefin, the low boiling component (below 180°) of 51.2% and the high boiling residue of 22.3% are considerably greater, so that the portion for the detergent group (oxo detergent range) amounts to only 26.5%. It should be taken into account that with the CO/H₂ synthesis product the fraction range is somewhat narrower (180-340° as compared to 175-340° with the Ruhrchemie primary olefin); however, the results were changed very little by this factor. The olefin content of the oxo detergent range is higher, having an average value of 46.1%.

N. W. Sy.-Produkt (Leuna)
 CO/H_2 SYNTHESIS PRODUCT (LEUNA)

BM 3
 Fig. 3



Based on the total product, an olefin content in the oxo-detergent range of 12.15% is obtained.

As to the oxability, the same conditions hold as for the Ruhrchemie primary olefin. In the direct sulfonation of the oxo conversion product, alcohols of too short a chain length (C_8-C_{11}) are also sulfonated as is the case with the primary olefin; these short chain alcohols amount to 9.1% of the total alcohol (i.e. primary alcohol + oxo alcohols). By assuming a 10% increase in weight in the oxation, and on the basis of the analytical examination, the alcohol distribution represented in Figure 4 is obtained. Before the direct sulfonation, however, this product requires, because of its ester content, a saponification, because otherwise during the neutralization of the sulfonation product portions of the esters might be saponified, thus leading to the formation of low molecular acid salts of the fatty acids. Removal of the esters by hydrogenation would also be practicable with a suitable catalyst, simultaneously with the oxo-aldehyde hydrogenation. By applying these measures, the primary alcohol and short chain alcohol (C_8-C_{11}) content is considerably increased.

Synol Cyclic Process Product (Leuna)

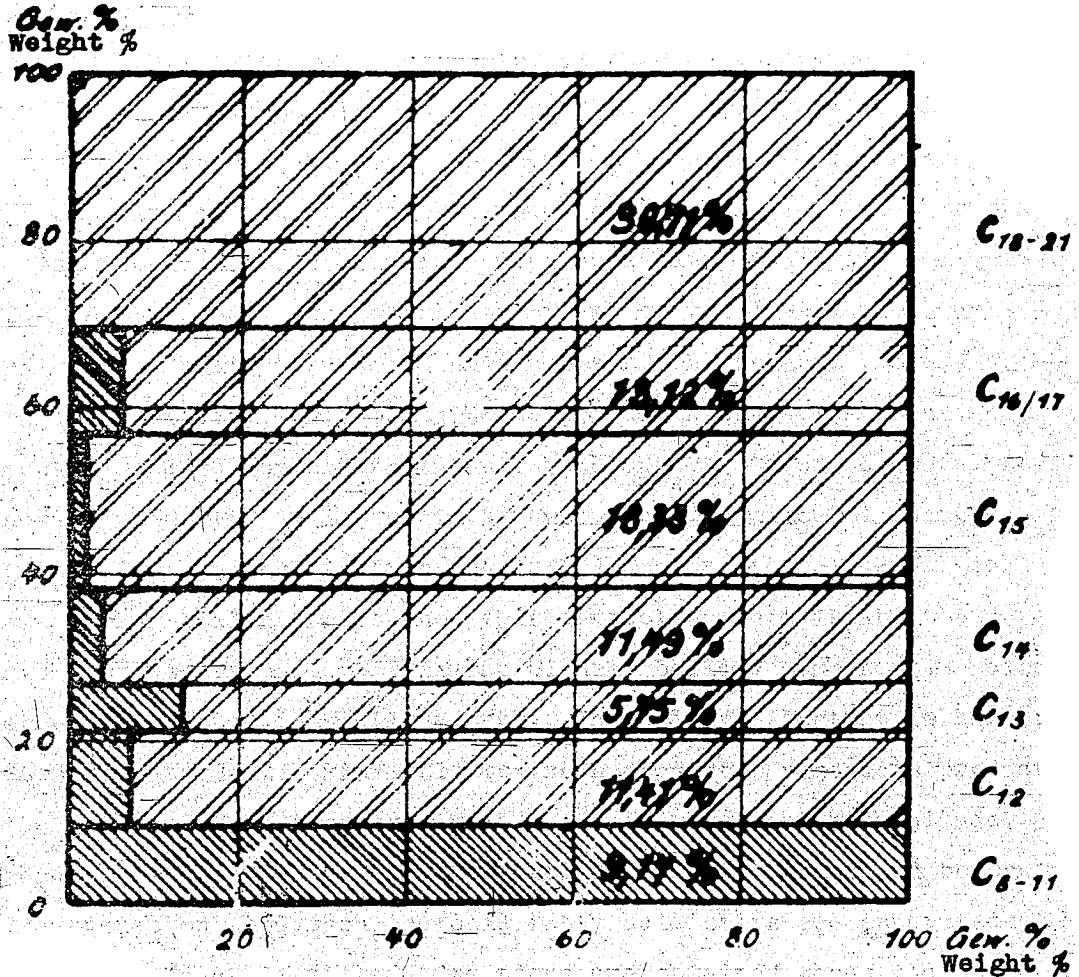
Method of Preparation:

This product is prepared by the reaction of carbon monoxide with hydrogen over highly active, fine grain iron catalyst. The synthesis temperature was 183°C, the pressure 20 atm., and the gas throughput as computed on the basis of the catalyst volume, 1:2700. The gas is recycled, as may be seen from the high throughput. Owing to the high gas velocity, the synthesis products were

Zusammensetzung der Gesamtalkohole nach Oxidierung des breiten Bandes 180-340°C (Oxowaschmittelbereich) von N.W. Sy-Produkt (Leuna)

COMPOSITION OF THE TOTAL ALCOHOLS AFTER OXATION OF THE
WIDE BOILING RANGE 180-340°C (OXO DETERGENT RANGE)
OF HYDROCARBON SYNTHESIS PRODUCT (LEUNA)

Bild 4
Figure 4




Primäralkohole
Primary Alcohols

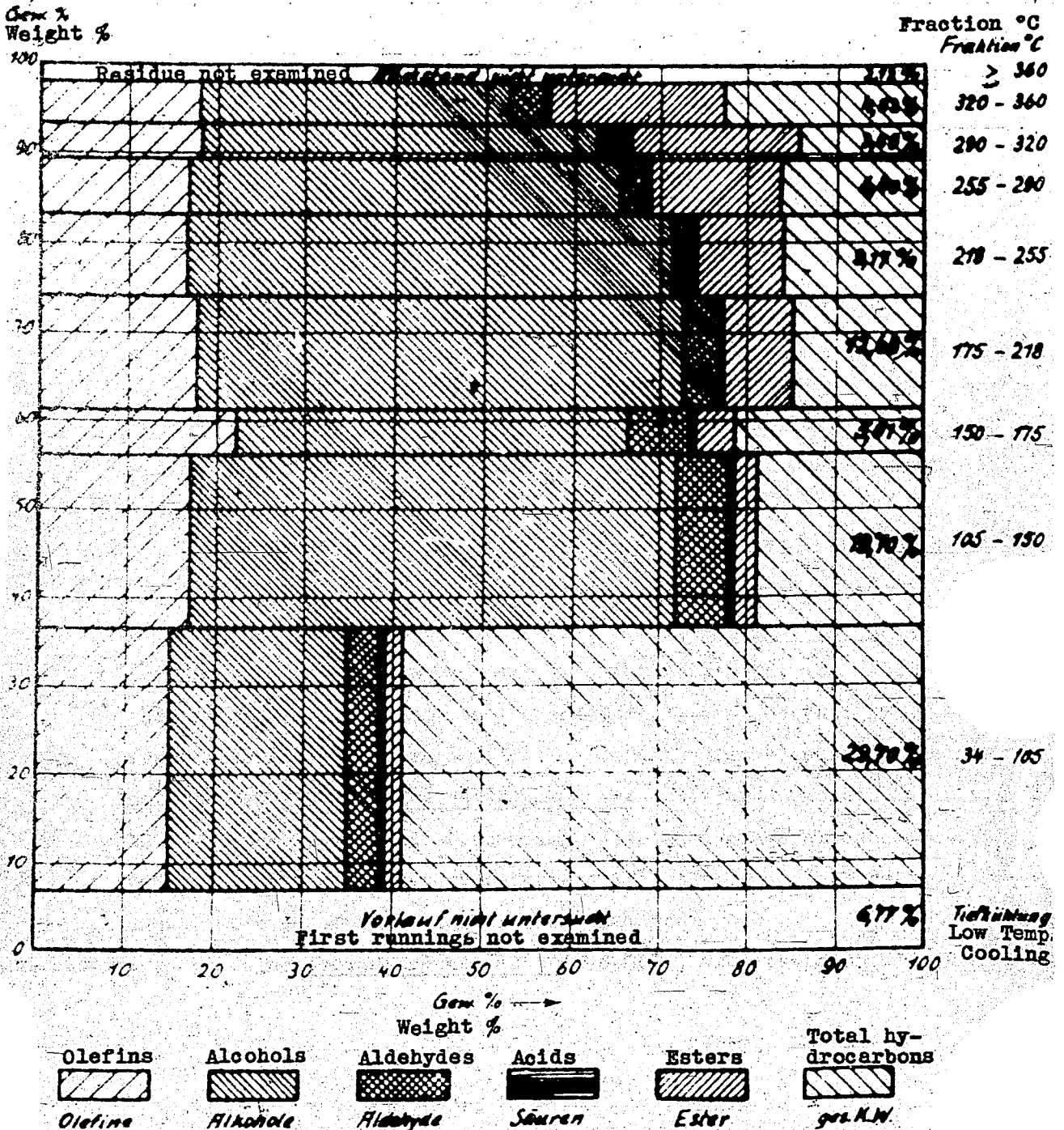

Oxoalkohole
Oxo Alcohols

removed from the catalytic chamber with great rapidity and thus the alcohols, apparently formed as primary reaction product, were removed unchanged from the reactor. The main portion of the synthesis product leaves the reactor in the vapor phase, together with the gas, and is subsequently separated by cooling of the gas circulation system. A small portion of the synthesis product (ab. 10%) precipitates in liquid form on the catalyst (reactor paraffin) and is discharged from the reactor in already separated form. The product examined consists entirely of the liquid portion discharged by the reactor, without gasol or product water. The results may be seen in Table 4 (see p. 19) and Figure 5 (p. 20). In this synthesis, one has to deal mainly with oxygenated synthesis compounds. Due to this fact, considerable portions of the lower molecular oxygenated compounds formed during the synthesis are, because of their solubility, dissolved in the product water. The amount of such dissolved components amounts to about 25-30% of the total reaction product. It is for this reason that the alcohol content of the low boiling fraction (34-105°C) amounts to only 20%. In the higher boiling fractions, this alcohol content is about 55%, and then decreases to 35% in the highest boiling component. Acids are present only in small amounts. The aldehyde content is higher, amounting to 3-7%. Similarly to the hydrocarbon synthesis product, the ester content increases with increasing molecular magnitude, reaching at times 20%. If the synol product is saponified before fractionation, and then the acid fatty acid salts are separated and the product distilled, fractions are obtained whose alcohol content is increased by the alcohols coming from the esters. This,

Synolkreislaufprodukt (Leuna)

SYNOL CYCLIC PROCESS PRODUCT (LEUNA)

Bild 5 zu Tafel 4
Fig. 5 for Table 4



for instance, may be seen from Table 5.

Table 5

Fraction Temp.	Without saponification				After saponification			Alcohol increase in %
	OH-No. theor.	OH-No. found	Ester No.	Alco- hol %	OH- No.	Ester No.	Alco- hol %	
175-218°	410	226	26	55	271	1	66	20
218-255°	340	187	28	55	225	0	66.2	20
255-290°	290	140	37	48.5	150	0	51.7	6.6

In the first two fractions (Table 5), a 20% increase of the alcohol content occurs. In the third fraction however, this increase amounts to only 6.6%. This leads to the conclusion that, by ester saponification mainly the short chain alcohol contents increase. With the detergent alcohols, an average increase of 5%, and not more, of the alcohol content may be assumed when saponification takes place.

The olefin content, as seen in Table 4, lies substantially lower and amounts on the average to about 16.8%. The component absorbed in phosphorus sulfuric acid, i.e. the sum of the oxygenated compounds + the olefins, amounts to almost 80%. The low value in the first fraction is due to the smaller alcohol content, since the lower alcohols are contained in the product water because of their solubility. The primary detergent range (255-360°) amounts to 14.8% of the total product examined, with an average alcohol content of 43.2%. The primary detergent alcohols C₁₂-C₁₈ therefore amount to 6.4% of the total product examined.

The oxo detergent range (175-360°) amounts to 36.65% of

the product examined, with an average olefin content of 17.3%. Calculated against the total quantity of product examined, the olefin content useful for oxation into detergent alcohols amounts to 6.35%. The low boiling components (below 175°) with 61.2% are high indeed, whereas the residue above 360° is very small with 2%.

After oxation of the wide boiling component 175-360° (oxo detergent range) and during the sulfonation which follows that portion of the primary lower alcohols present in the fractions 175-255°, whose chain length (C₇-C₁₁) is too short for the detergent group, is collected together with the other alcohols. On the basis of analytical examinations it was found that with the synol product this short chain alcohol content is considerable, amounting to 46.7% of the total alcohols (i.e. primary alcohol present + newly formed alcohol obtained from the oxo synthesis) in the oxo detergent range. This is illustrated in Figure 6. From this figure one may furthermore get a picture of the alcohol distribution according to the C number, and the primary alcohol content alongside the oxo alcohol in the higher molecular alcohols. Here again, the same assumptions as to the weight increase caused by the oxation were applied, as had been used in the previous products.

Because of the large portions of short chain alcohols, a separation of these alcohols by distillation after oxation seems practicable. An alcohol mixture is then obtained, the composition of which is illustrated in Figure 7. Besides 47.73% primary alcohol (synol alcohol), the mixture also contains 52.27% oxo alcohols. The primary alcohol content (i.e. synol alcohol content) in the primary detergent range increases by a maximum of 5% (see p. 15)

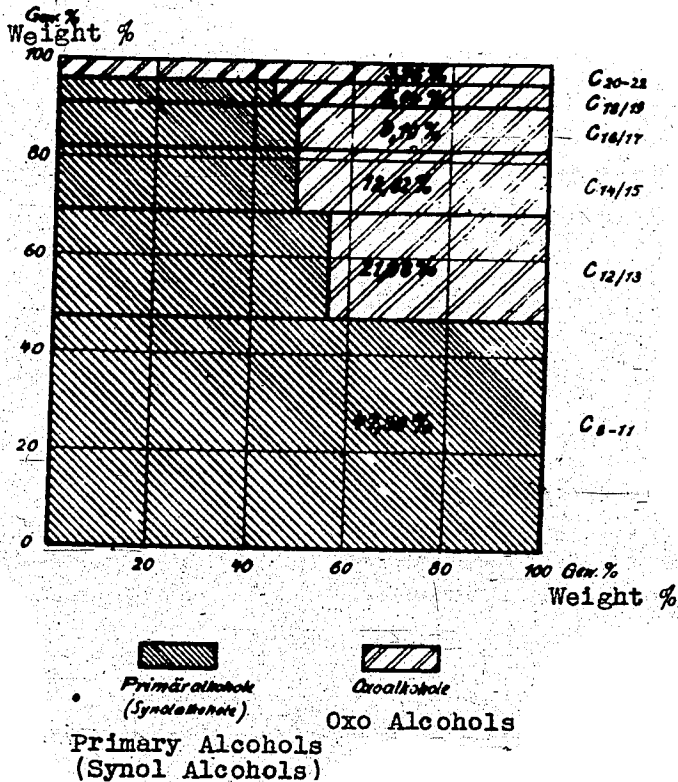
- 14 -

wichtigste-nahme durch die (hier)
geleckt.

COMPOSITION OF THE TOTAL ALCOHOLS
after oxation of the wide boiling fraction 175-360° (oxo detergent
range) of Synol cyclic process product (Leuna)

*Zusammensetzung der Gesamtkohole
nach Oxierung des breiten Bandes 175-360° C (Oxowaschmittelbereich)
von Synolkreislaufprodukt (Leuna)*

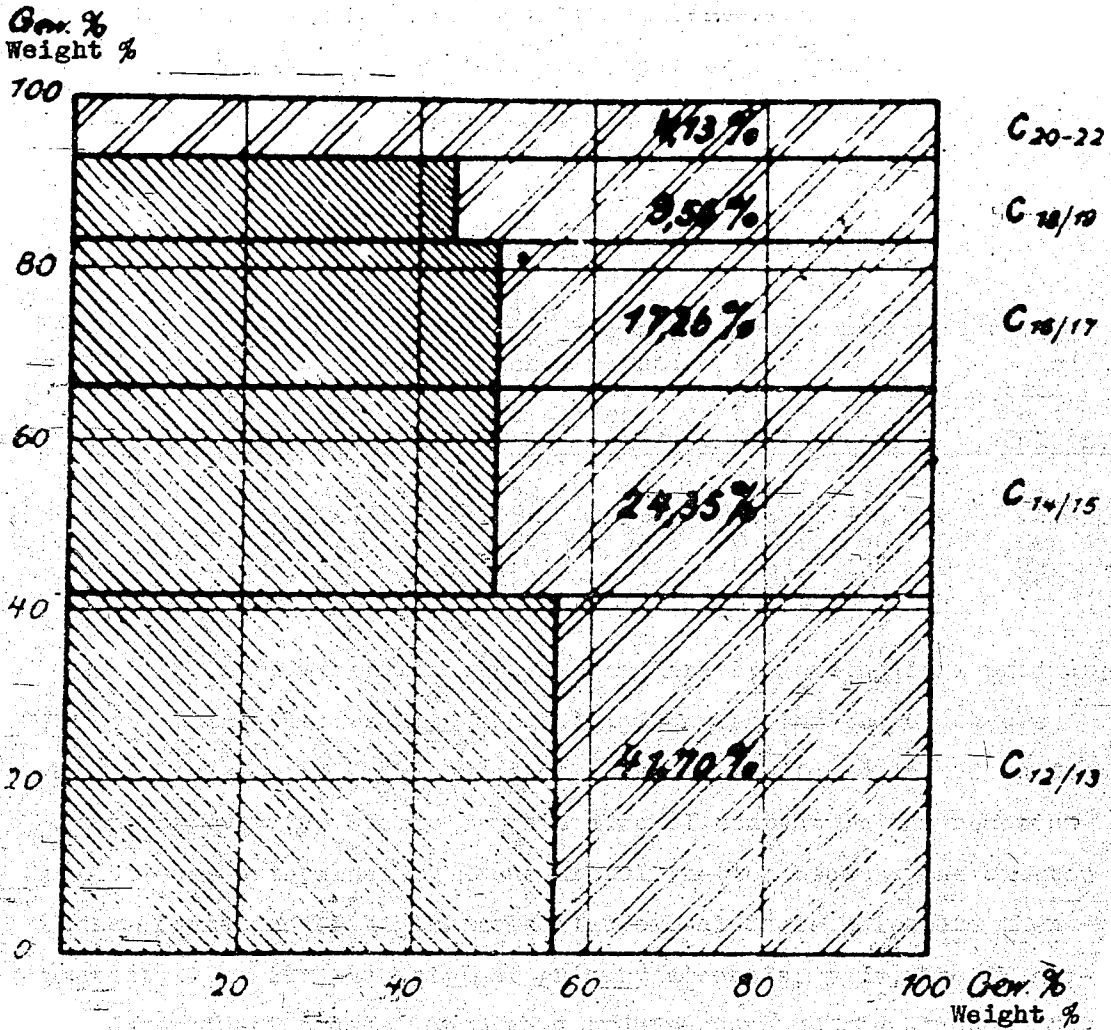
Bild 6
Figure 6



Zusammensetzung der Gesamtalkohole
 nach Oxidation des breiten Bandes 175-360°C v. Synoltriallaufprod.
 und nach Abtrennen der niederen Alkohole C₈-C₁₁ d. Destillation

COMPOSITION OF THE TOTAL ALCOHOLS
 after oxidation of the wide boiling fraction
 175-360° of synol cyclic process product
 and after separation of the lower
 alcohols C₇-C₁₁ by distillation

Bild 7
 Figure 7



Primary Alcohols
 (Synol Alcohols)



Primäralkohole
 (Synolalkohole)

Oxo Alcohols



Oxoalkohole

when the product is saponified for removal of the esters before oxation. In this case, the proportion between primary alcohol and oxo alcohol in the detergent range would be changed very little. Thus, by means of oxation, an extremely large increase of the detergent alcohols is achieved.

The total alcohol content was determined, both before and after oxation, by the OH number and also by the chlorosulfonic acid sulfonation. For the fractions above 175°, the results are tabulated in Table 6 below:

Table 6

Fraction	Before Oxation					After Oxation			
	Density at 20°C.	OH- No.	CO- No.	% alcohol based on OH No.	% alcohol based on sulfon.	Density at 20°	OH- No.	CO- No.	% alcohol based on sulfon.
175-218	0.797	225	15.5	55	57	0.813	293	0	71
218-255	0.810	187	9.0	55	58	0.821	234	0	74.5
255-290	0.817	140	8.0	48.5	51.5	0.826	160	0	69
290-320	0.820	114	8.0	44.5	43	0.833	135	0	76
320-360	0.823	75	7.0	35	39	solid	94	0	61

The oxation leads to a considerably more uniform product, by converting olefins into alcohols, and removing the aldehydes and/or the ketones. This product consists, as found in the sulfonation, of over 75% alcohol. This alcohol content in the reaction product was determined by means of sulfonation because the oxation causes formation of higher molecular oxo-alcohols which are then present alongside the original primary alcohols; thus, the OH number determination does not give a true picture of the alcohol content in this case.

In order to avoid any possible misunderstandings, it should be pointed out that the data tabulated in Table 6 and the graphical representations 6 and 7 do not constitute a contradiction. From Table 6 it appears that by the oxidation the alcohol content increases by only one half, whereas in Fig. 6 and 7 primary alcohols and oxo alcohols in the detergent range are indicated in equal quantities. Attention is also called to the fact that in Figure 6 and 7 alcohols of the same C-number are put next to each other, whereas in Table 6 the oxo alcohol which stems from an olefin of the same boiling behavior as the primary alcohol is contained. Thus, this oxo alcohol contains about 4 C-atoms more than the accompanying primary alcohol. The boiling range which contains the primary alcohol of the same C number is, however, narrower because with increasing C numbers the fractions are narrowed down; also, the primary alcohol content will be lower. (See Figure 5: decrease of the primary alcohol content with increasing C-number in the detergent range). Therefore, an about equal concentration of oxo alcohol and primary alcohol of the same C-number in the detergent range (Fig. 6 and 7) results. This is clearly seen in Figure 5 where the area which is limited by olefins above 175° (i.e. those which yield detergent oxo alcohols) is approximately equal to the area covered by the primary detergent alcohols (above 255°) and the aldehydes.

The conversion of the originally present primary aldehydes into alcohols during the hydrogenation which follows the oxo synthesis, causes no great change in the boiling behavior of the detergent range, so that in Table 4 and Figure 5 the aldehyde contents are to be added to the primary alcohol content if the product is

subjected to hydrogenation treatment, as is the case in the oxo synthesis.

Michael Products (Ludwigshafen)

Method of Preparation

In contrast to the other products, this particular product is prepared in the liquid phase with slurried iron catalyst. The hydrogenation of the carbon monoxide does therefore not occur in a tubular reactor but rather by leading the synthesis gas, finely divided by means of porous plates, through a pressure container filled with catalyst slurry. Pressure = about 15-20 atm., synthesis temperature = 230-270°.

Analytical Composition

The analytical composition illustrated in Figure 8 and Table 7 is the result of a verbal communication from Dr. Michael, concerning the proportions of benzine and intermediate oil in the collected product, and the amount of paraffin (residue); and also, of our own analyses performed on a benzine and an intermediate oil obtained from this synthesis.

The alcohol content in the oxo detergent range (175-360°) decreases from 25% to 1% in the highest boiling fractions. The aldehyde content decreases from 2% to 0. Acids are present only in small amounts. The ester content, on the other hand, increases with increasing molecular weight, just as it did in the previous cases. It increases from 8% to 19%. The olefin content falls off, from 48% to 32% in the high boiling fractions.

The component boiling below 175° amounts to 46.5% and was not further examined. The oxo detergent range (C₁₁-C₂₁) totals

ementsproband nicht in einem Röhrenofen, sondern durch Durchleiten des durch Schaumplatten fein verteilten Synthesegases durch einen mit der Kontaktaufschlammung gefüllten Druckbehälter. Der Druck beträgt 15 - 20 Atm., die Synthesetemperatur liegt zwischen 230 und 270°C.

Analytische Zusammensetzung

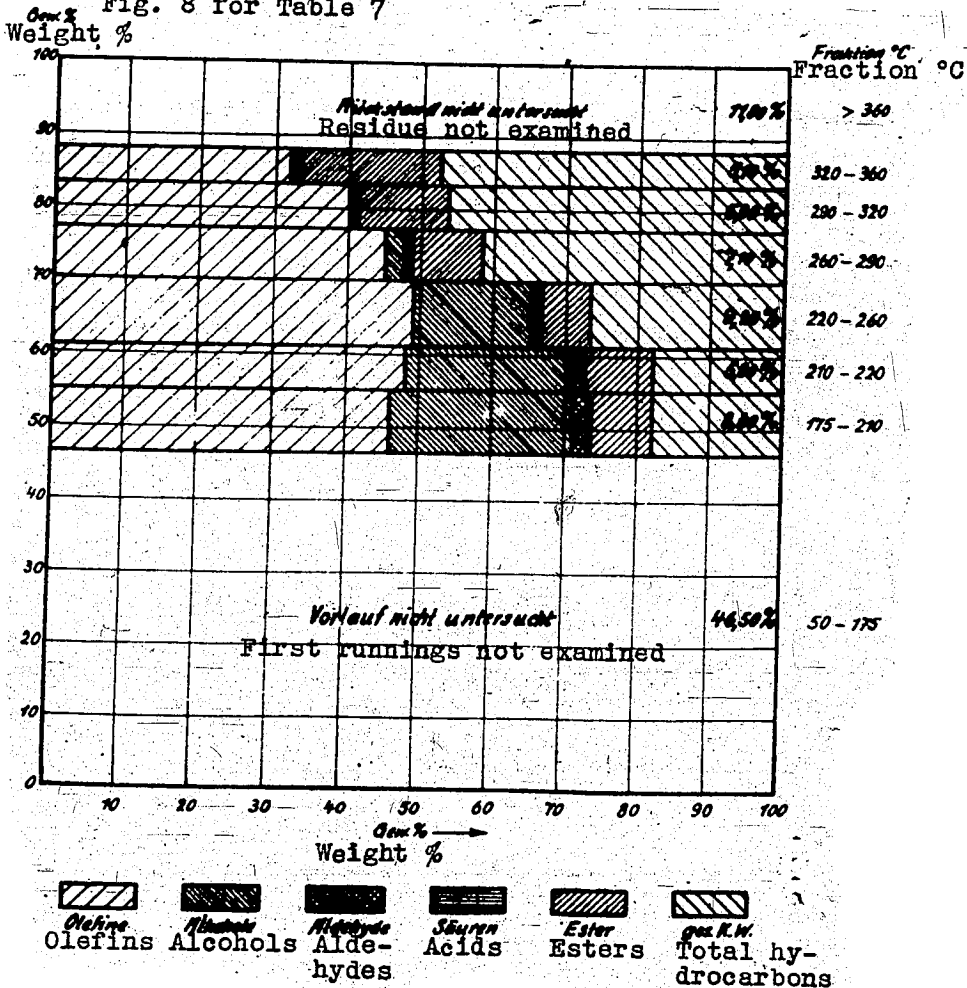
Auf Grund mündlicher Mitteilung Dr. Michaelis bezüglich des Anfallverhältnisses von Benzins und Mittelöl und der Anfallmenge an Paraffin (Rückstand) und durch unsere analytischen Untersuchungen eines aus dieser Synthese stammenden Benzins und Mittelöls ergibt sich die aus Tafel 7 und Bild 8 ersichtliche Zusammensetzung.

Michaelprodukt (Ludwigshafen)

MICHAEL PRODUCT (Ludwigshafen)

Bild 8 zu Tafel 7

Fig. 8 for Table 7



41.7%, the residue 11.8%. The average olefin content of the oxo detergent fraction is 44.4%. Calculated against the total product, the olefin content is found to be 18.52% ($C_{11}-C_{21}$).

Oxation of the component 175-360° (oxo detergent range) leads, if the same assumptions as to weight increase are maintained, to an alcohol mixture containing 19.35% primary alcohols of too short a chain length (C_7-C_{11}). These had to be removed by distillation, just as had been the case with the synol product. The composition of the alcohols and their distribution according to their C number which is determined on the basis of analytical examinations of the oxo synthesis initial product, is shown in Figure 9.

The primary alcohol content is only very small in the higher alcohols from C_{12} on upwards; however, this alcohol content would be substantially increased in case of ester saponification and/or ester hydrogenation.

The convertibility of the Michael products in the oxo reaction corresponds in all its aspects to that of the primary olefin. (Alcohol yields average 95-96%.) In the Michael products too, removal of the esters is necessary for reasons already described; this removal of the esters may be accomplished by saponification or ester hydrogenation.

Lurgi Synthesis Product (Dr. Herbert)

In connection with this report, another carbon monoxide hydrogenation product should be described, which is prepared in an experimental reactor by Dr. Herbert - Lurgi in the A.S.W.* This product too is prepared by a medium pressure synthesis over iron precipitate catalyst and with recycle gas flow. The exact synthesis

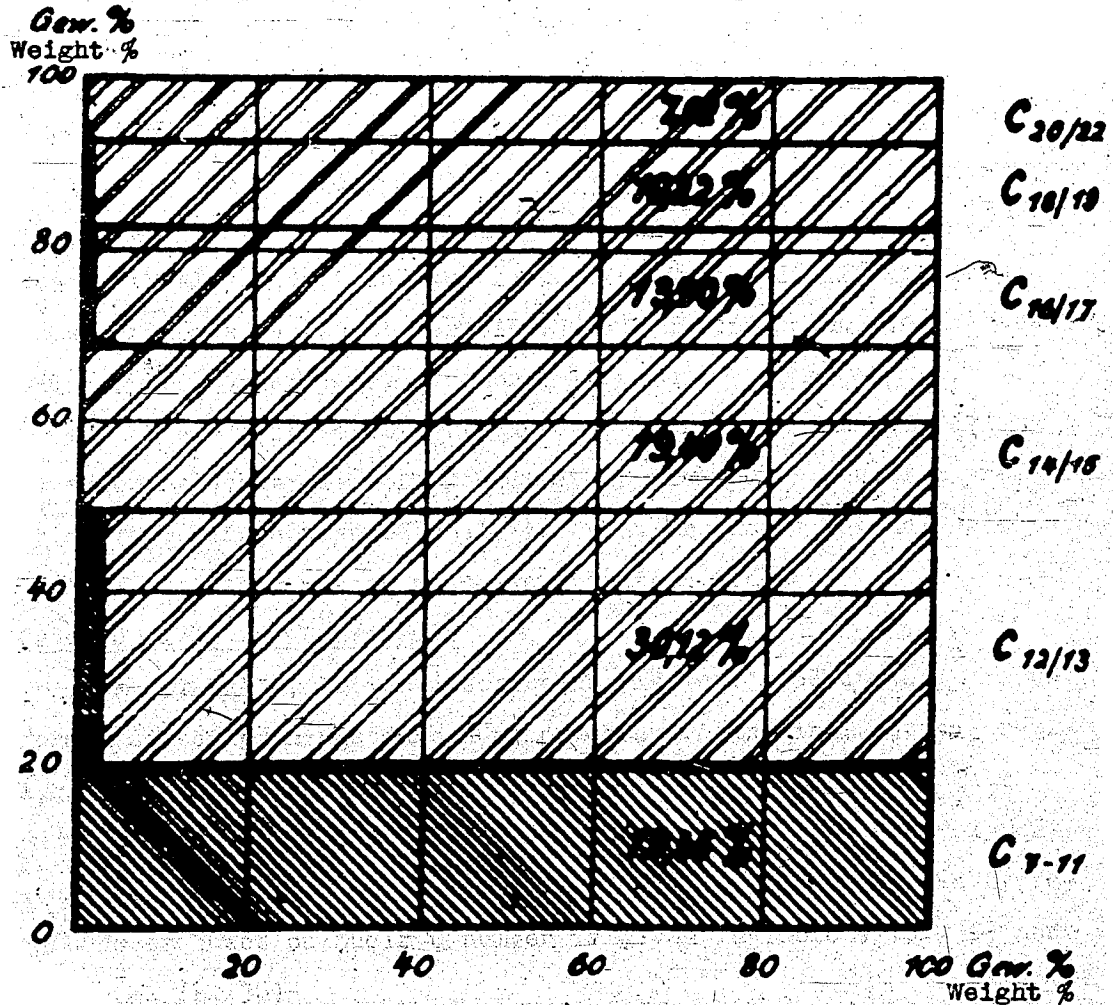
*A.S.W. = probably Ammonia Synthese Werk = Ammonia synthesis plant (Transl.)

Zusammensetzung der Gesamtalkohole nach Oxidation des breiten Bandes 175-360° (Anstrichmittelsort) von Michaelprodukt (Ludwigshafen)

COMPOSITION OF THE TOTAL ALCOHOLS
after oxidation of the wide boiling range 175-360°
(oxo detergent range) of Michael
synthesis product (Ludwigshafen)

Bild 9

Figure 9



Primary Alcohols



Primäralkohole

Oxo Alcohols



Oxoalkohole

conditions, as well as the method of separation, are not known to us in detail, so that we are able to give only the results of a primary distillate up to 320°. Only the oxo detergent component was subjected to examination. The data obtained are given in Table 8 (see p. 33) and illustrated in Fig. 10 (see p. 34).

The product contains about 5% alcohols, small amounts of acids and no aldehydes. The low ester content, especially in the higher boiling fractions, is remarkable. The olefin content decreases from 51% and 54.4% in the first two fractions respectively, to 45.3%. The average olefin content of the oxo detergent range is 51.6%. The product resembles to a certain extent the hydrocarbon synthesis product and the Michael product. It differs from these products in its higher olefin content and in its lower ester and alcohol content. Furthermore, it contains no aldehydes.

As to its oxability, no experiments could be performed because the quantities of product available were not sufficient. It may however be assumed that its behavior should be analogous to that of the other carbon monoxide hydration products.

Cracked Olefin of Ruhrchemie

Finally, let us describe an olefinic product which is not formed directly in the carbon monoxide hydrogenation, but by cracking of the Fischer synthesis products (Paraffine-Gatsch). This product consists uniformly of hydrocarbons and contains no oxygenated compounds. Its composition and the distribution of the hydrocarbons as based on their C-number is given in Table 9 (p. 35) and Figure 11 (p. 36).

The olefin determination of this product was carried out

Lurgi-Syntheseprodukt
LURGI SYNTHESIS PRODUCT

2 -

Bild 10 zu Tafel 8

Fig. 10 for Table 8

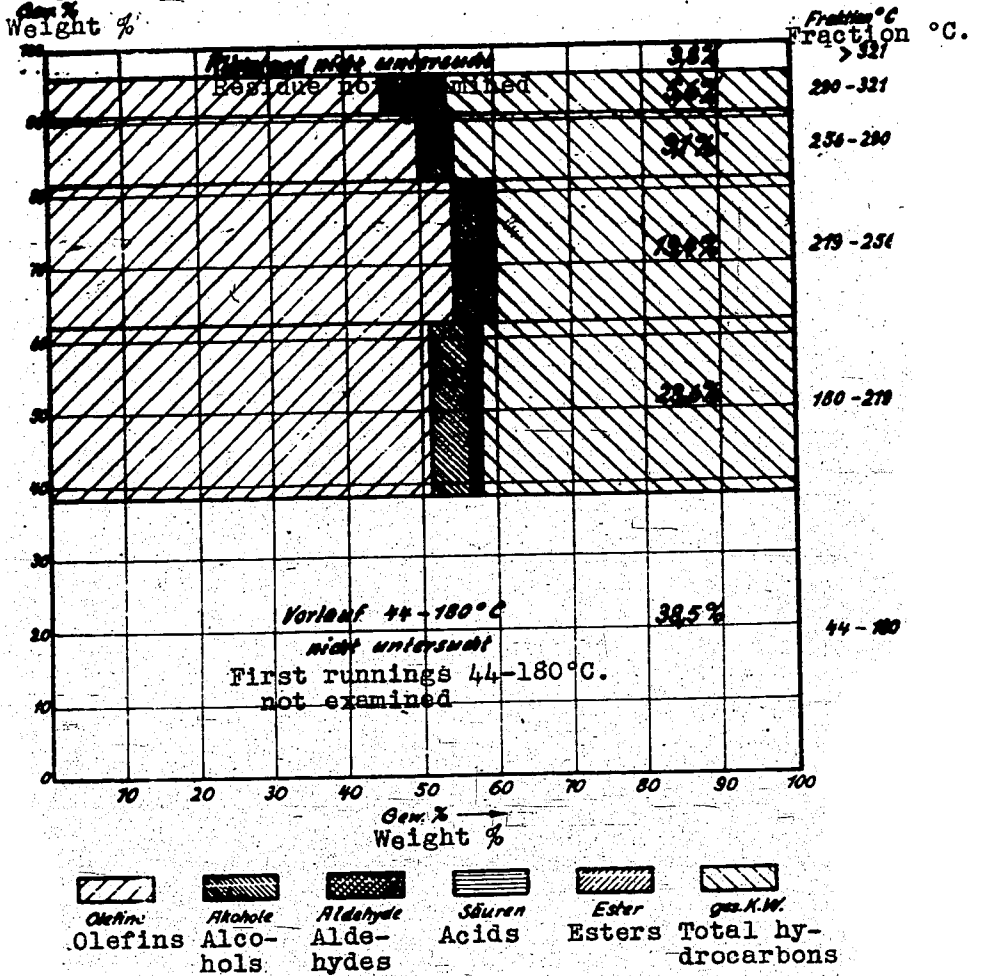


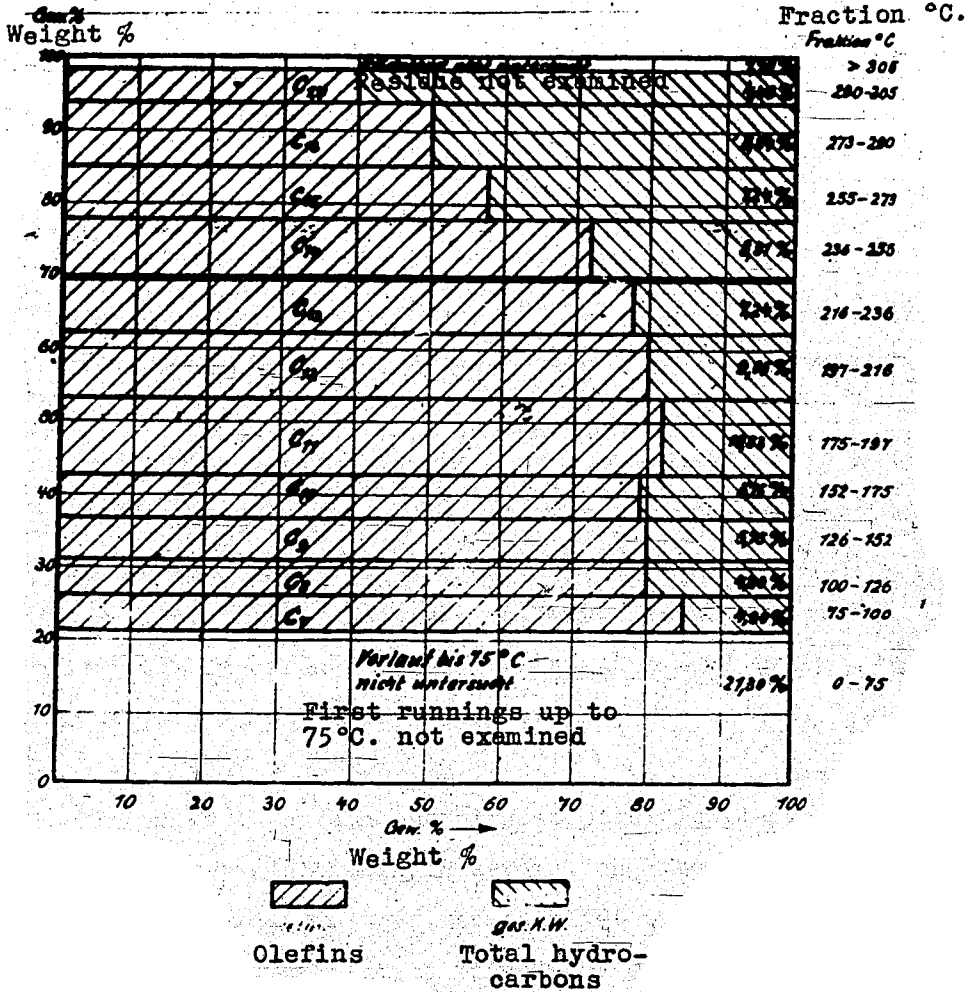
Table 9
Ruhrohemis Crackolefins

Fraction	Temperature at 760 mm.	Amount in Weight %	Spec. Gravity at 20°C.	SPL %	C-Number	Iodine No. for 100% Olefin	Iodine No. Huns	Olefin % Huns	Bromine No. Klein	% Olefin Klein	% Olefin Average
First Runnings	- 75	21.3	-	-	below 7	-	-	-	-	-	-
1	75-100	4.9	0.701	84	7	259	225	87	217	84	85
2	100-126	4.9	0.722	76	8	226	190	84	183	81	80
3	126-152	5.75	0.735	75	9	201	171	85	163	81	80
4	152-175	5.75	0.745	75	10	181	156	86	139	77	79
5	175-197	10.53	0.755	82	11	165	139	83.5	134	81	82
6	197-216	9.05	0.761	77	12	151	121	80	124	82	80
7	216-236	7.24	0.772	75	13	140	108	77	113	81	78
8	236-255	8.31	0.775	69	14	130	96	74	94	72	72
9	255-273	7.24	0.776	57	15	121	75	62	68	56	58
10	273-290	6.84	0.782	47	16	113	60	53	57.5	51	50
11	290-305	4.48	0.785	40	17	106	44.5	42	41.5	39	40
Residue	above 305	1.7	-	-	above 17	-	-	-	-	-	-

Krackolefin der Ruhrchemie
RUHRCHEMIE CRACKOLEFINS

Bild 11 zu Tabelle 9

Fig. 11 for Table 9



by the method of Klein and Hanus. However, also the phosphoric-sulfuric acid absorption test gives very accurate results. This olefin, which was also oxated on a larger scale by the Leuna continuous process, is over 95% convertible.

The high olefin content of this olefin, which lies around 80% in the members up to C_{13} , is noteworthy indeed.

Comment and Interpretation of the Results

The analytical results obtained from the carbon monoxide hydrogenation products of different origin and preparation were compared as to their suitability for use as initial products for the oxosynthesis of detergent alcohols. From the various illustrations which give the composition of the examined products, one can see that:

1. Carbon monoxide hydrogenation products prepared over cobalt catalyst are more uniform in their composition and therefore are processed more easily than the iron catalyst products.

2. The sum of the olefins + the oxygenated compounds, which is of decisive importance in the further chemical processing, is highest in the synol, where its value exceeds 80% in most fractions.

3. In order to obtain the highest possible yield of valuable chemical compounds by simple separation, the primary synthesis products resulting from the iron catalyst synthesis must be subjected to a suitable treatment by which they are rendered more uniform. The most practicable treatment of such nature is first of all the oxo process, which not only converts the olefins but also the aldehydes, into alcohols. The esters must be removed.

either by previous saponification or by hydrogenation treatment following the oxo synthesis. The alcohol contents would thus be increased in proportion to the ester content. With the synol cyclic process product, the alcohol content would increase by an over 10% average of the previously present alcohols, when the esters are subjected to the hydrogenation split.

Another method for rendering the synthesis products more uniform would be to dehydrate the product beforehand; thus, a pure paraffin-olefin mixture is obtained. This could then be processed further by oxidation. The following Table 10 (see p. 39) gives information concerning the conditions for preparation, the composition, and the possible detergent alcohol yields which may be achieved with the synthesis products examined.

From Table 10 it may be seen that the first runnings are especially copious in the synol product. In order to clarify this point, the relations between the amounts of first runnings are compared in Fig. 12 (p. 40) and it appears that the first runnings of the synol cyclic process product consist of appreciable amounts of alcohols.

The oxo detergent range, on the contrary, is substantially greater in the Ruhrchemie primary olefin than in the Leuna iron catalysis products. The iron catalysts being employed at this time by Leuna seem to yield an exceptionally small intermediate fraction. The Michael product, as far as its oxo detergent range is concerned, lies somewhere in between the Leuna iron catalyst products and the Ruhrchemie cobalt catalyst primary olefin. This is illustrated in Figure 13 (p. 41), which also gives the olefin and alcohol content

Table 10

Catalyst	Kind	Ruhrchemie Inc. Primary Olefin	Hydrocarbon Synth. Product, Leuna	Michael Product Ludwigshafen	Synol Cyclic Process Product Leuna, With Reactor Paraffin and Water Soluble Components	Synol Cyclic Process Product Leuna, With Reactor Paraffin and Water Soluble Components
	Form	CO precipitate catalyst	Fe catalyst	Carbonyl-iron catalyst	Fine grain iron catalyst	Fine grain iron catalyst
		Solid	Solid	In oil sludge	Solid	Solid
Synthesis Conditions	Synthesis Temperature	180-190°	270°	230-270°	183°	183°
	Synthesis Pressure	8-12 atm.	19 atm.	4.5-20 atm.	20 atm.	20 atm.
	Gas Flow	Cycle	Straight passage	Straight passage	Cycle	Cycle
Boiling Spectrum	First Runnings up to 175° (180°)	25.2%	51.2%	46.5%	61.2%	64.6%
	Oxo Detergent Range	64.9%	26.5%	41.7%	36.65%	26.55%
	Residue	9.8%	22.3%	11.8%	2.1%	8.85%
Oxo Detergent Range	Olefin Content	31.1%	46.1%	44.4%	17.31%	17.31%
	Alcohol Content	8.3%	7.26%	12.45%	50.2%	50.1%
	Olefin Content of Total Product	20.3%	12.15%	18.52%	6.35%	4.6%
Primary Detergent Range	Alcohol Content of Total Product	5.39%	1.92%	5.2%	18.4%	13.3%
	Amount in % by Weight	29.7%	13.19%	18.1%	14.6%	11.08%
	Alcohol Content of Total Product	7.24%	3.66%	1.41%	43.2%	43.2%
Detergent Alcohols from Cl ₂ on up, in % of the Total Product	Originally Present (Primary)	2.15%	0.5%	0.26%	6.3%	4.8%
	Prepared by Oxidation	22.22%	13.37%	20.37%	6.99%	5.06%
	Total Detergent Alcohols	24.37%	13.87%	20.63%	13.37%	9.86%

FIRST RUNNINGS IN WEIGHT %

Verlauf in Gew %

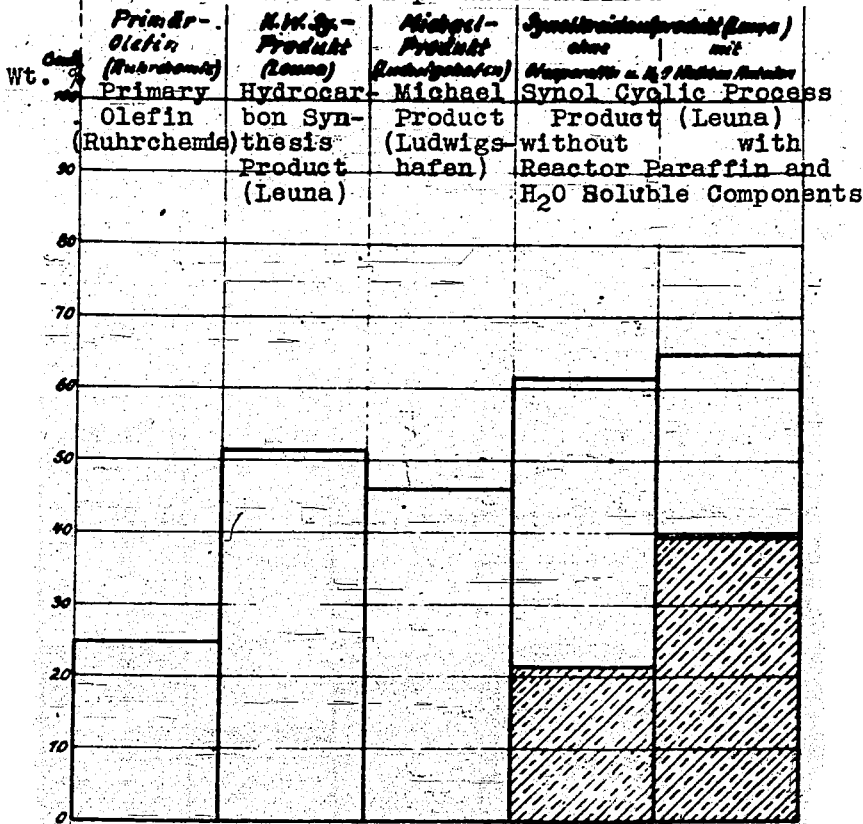
27


(Benzinfraktion ab etwa C₁₀-Olefin)

bezogen auf die jeweils untersuchten

Gesamtergebnisse.

Bild 12 (Benzine Fraction up to and including C₁₀ Olefin), of the total product examined



 niedrig molekulare Alkohole unterhalb des Oxo-waschmittelbereichs sind
 Low molecular alcohols, boiling below the
 Oxo detergent range

OXO DETERGENT RANGE IN WEIGHT %

Oxo-Waschmittelbereich in Gew. %

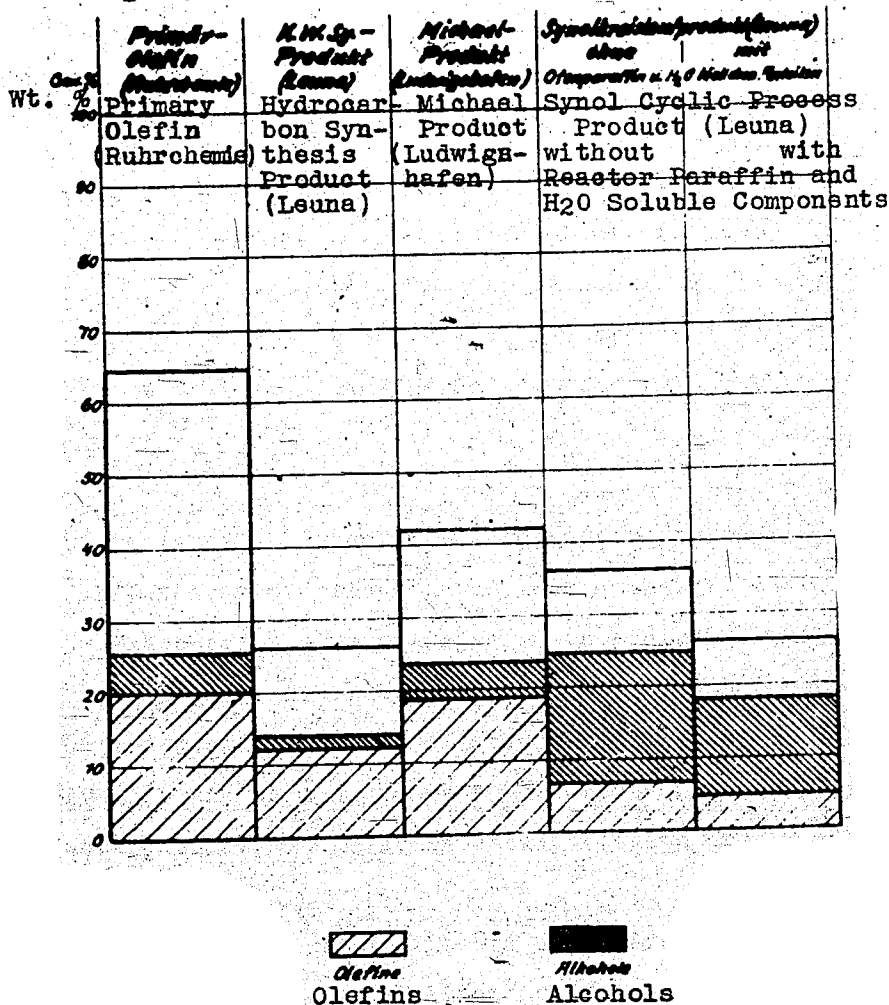
(Dieselfraktion oberhalb C₁₀-Olefin)

bezogen auf die jeweils untersuchten

Gesamtprodukte.

3 -

Bild 13 (Dieseloil Fraction Above C₁₀-Olefin)
Fig. 13 of the particular total product examined



of this range.

The last three rows of values in Table 10 constitute the amounts of detergent alcohols based on the total product; the table is illustrated by Figure 14 (p. 43).

The total detergent alcohol yield is highest with Ruhr-chemie primary olefin and Michael product. Despite the fact that the synol synthesis yields products of very high alcohol concentration, the detergent alcohol yield is low because of the so far not very satisfactory quantitative amount of intermediate component. By oxidation of the synol product, the detergent alcohol component can be doubled, and yet even then the total detergent alcohol yield is only about 10% of the total reaction product. It is thus easily seen that the amount of intermediate component is of decisive importance for the yields one can achieve in the preparation of detergent alcohols.

Summary

Olefinic carbon monoxide hydrogenation products prepared by various different synthetic methods, and a thermal cracking product from Fischer-Gatsch were subjected to analytical examination and the degree of convertibility of their olefinic components in the oxo reaction was determined. In these studies, special attention was given to the boiling range to be used for the preparation of detergent alcohols. The most important results are summarized below:

1. Oxidation of the olefins is successful in all products, the conversion exceeding 95% in all cases.
2. The cobalt products are more uniform in their compo-

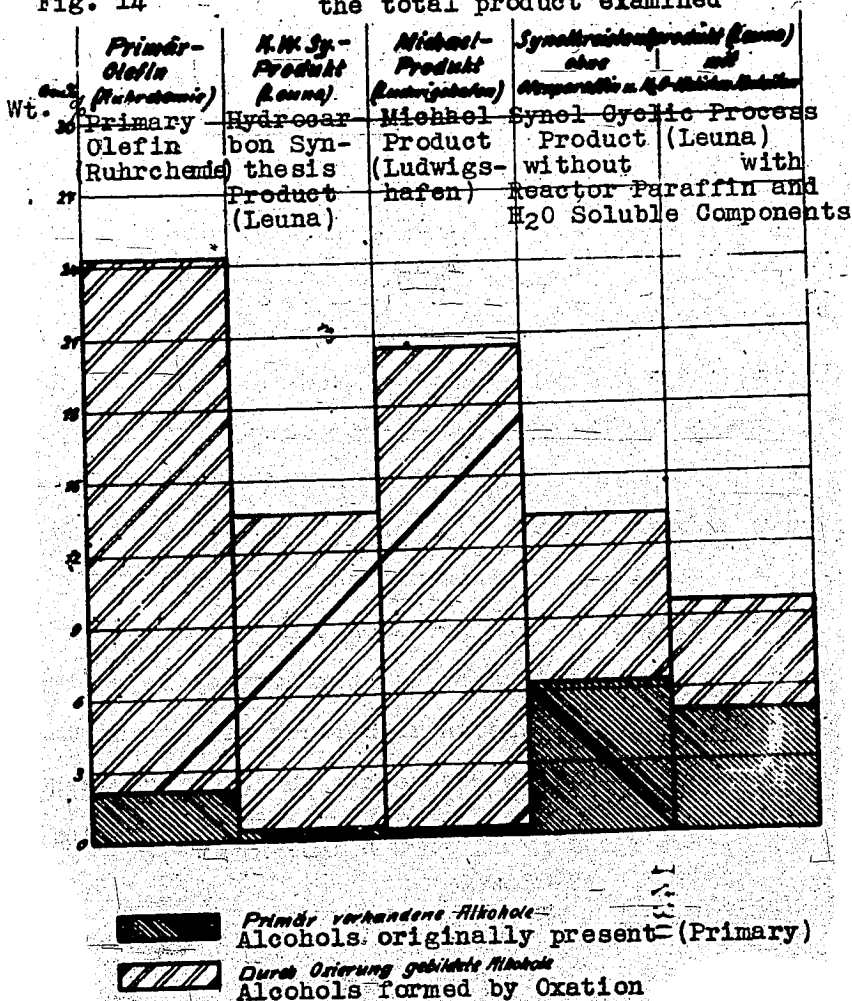
TOTAL DETERGENT ALCOHOLS IN WEIGHT %
Gesamtwaschmittelalkohole in Gew. %

- 29 -

*(Primär vorhandene und durch Oxidierung neu gebildete Alkohole
 einsch. C₁₂ aufwärts) bezogen auf die jeweils untersuchten*

Gesamterzeugnisse.

Bild 14 (Originally Present and Those Newly Formed
 Fig. 14 by Oxidation, Including C₁₂ and Upwards) of
 the total product examined



sition than the iron products, the former consist mostly of only olefins, paraffins and alcohols.

3. The iron products contain substantial amounts of acids, esters and aldehydes; they are therefore rendered more uniform by the hydrogenation which is connected with the oxation process; this facilitates their further processing.

4. The alcohols present after oxation (i.e. the original + the oxo alcohols) are appreciably less with the cobalt products than with the iron products; they reach a maximum value with Leuna synol product.

5. The fraction containing alcohols of such chain length as is necessary for their use as detergents is smaller in all the iron products, because the fraction corresponding to this chain length is smaller. The catalyst being used at this time by Leuna for the synol synthesis yields a "detergent fraction" which is so small that the detergent alcohol yield, even after oxation, is only about 10% of the total product of the synthesis; and this despite the fact that the alcohol component reaches about 70%.

In any further work concerning the preparation of detergent alcohols from carbon monoxide hydrogenation products it is therefore important to pay particular attention not only to the alcohol component and to those components which are convertible into alcohols, but also to the boiling spectrum.

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