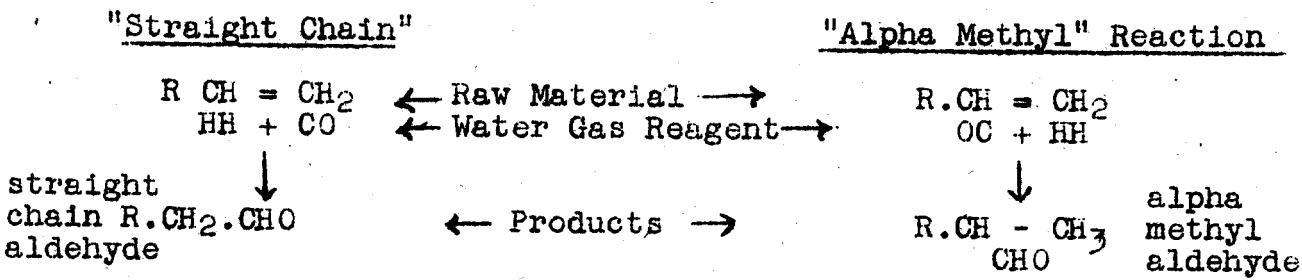
F. CHEMISTRY OF THE PROCESS

The typical reaction which occurs during the process may be symbolized in general terms in the formula below, where R is a radical.

1st Stage



2nd Stage

Raw Material (aldehyde from 1st stage) ⟶	R.CHO
Hydrogen Gas Reagent →	H H
Product Alcohol ⟶	$R.CH_2.OH$

The migration of the double bond which always occurs to a significant extent simultaneously with aldehyde formation may be indicated as a reaction preliminary to the first stage, thus:

alpha olefins ⟶ olefins with "middle" bond, i.e.,

$$CH_3(CH_2)\ x\ CH = CH_2 \rightarrow CH_3\ (CH_2)x\text{-}y.\ CH = CH(CH_2)y\ CH_3$$

After rearrangement, as portrayed, reaction at the double bond in the first stage may follow either of the courses indicated above. The higher the temperature, usually the greater the rearrangement.

While the U.S. Patent mentions Ketone formation and this was alluded to be in interviews the documents reviewed fail to be specific on this point. A viscous oil ("Dickol"), stated to be the result of some aldolization and Ketone Reaction, is mentioned as a by-product of 1-10% yield when C_7-C_{10} compounds are processed.

The rearrangement or isomerization of the double bond is an important feature of the reaction, as is the formation of alpha-methyl and indeed of alpha-alkyl branched products. In a rather comprehensive experiment with a specially purified dodecylene as raw material (14-638, August 21, 1942), the I. G. laboratories came to the following conclusions:

1. Mixtures of isomeric aldehydes, alcohols, and corresponding acids are obtained even when pure olefin bond is used as raw material.

2. Using an end double bond olefin as raw material, one obtains about 60% branching in the OXO process.

3. The building of branched compounds is due to the fact that double bond isomerization occurs during the OXO reaction. This is caused by cobalt carbonyl.

4. Not only are alpha-methyl compounds formed, but, in general, alpha-alkyl branched products are found. Because of this circumstance, the melting point of OXO acids made from the alcohols are substantially lower than the normal fatty acids with the same number of carbon atoms. The marked tendency of the soaps made from OXO alcohols to absorb water reflects this mixture of branched materials.

5. Isomerization and the OXO reaction proceed simultaneously, the latter probably with the greater velocity, so that the formation of branched products in the reaction forming aldehydes is not as great as might be surmised from the laboratory experiments on the isomerization of olefins in the presence of carbon monoxide--but in the absence of hydrogen.

6. Iron carbonyl also isomerizes olefins, but nickel carbonyl has no effect.

Table I (the next page) gives the experimental conditions used which led to the above conclusions.

The experiment with iron carbonyl had a more basic incentive than appears from what has been said to date. Aside from the OXO process to produce alcohol, the so-called Synol process using an iron catalyst was in a sense a competitive operation. This process will be reported in greater detail elsewhere, but in order to read the documents on the OXO process intelligently, some knowledge of the Synol process is necessary.

In brief, the Synol process consists in contacting synthesis gas, i.e., purified water gas as used in the normal Fischer process, with a specially reduced iron catalyst. A gas pressure of 20-25 atmospheres is maintained and a temperature of 185°-195°C. is used. The Synol process produces alcohol directly and thus reverts in a sense to the early work of Fischer (1923-1925), or might be looked upon as the OXO process under slightly different conditions applied to nascent olefins in situ. The reaction requires very careful temperature control and a large ratio of recycle gas to fresh feed. Though the major yield is of alcohol in the carbon atom range of C_4-C_8, some higher molecular weight alcohols are formed. Naturally, then, both economic and technical comparisons were continually drawn by the Germans between the OXO process and the Synol process for making higher alcohols.

TABLE I

EXPERIMENTS SHOWING MIGRATION OF DOUBLE BOND WITH HIGHER OLEFINS

Autoclave Charged with										
Dodecylene c.c.	Catalyst, Vol. or wt.	Reaction Temp.	Gas Used	Press. Atmos.	Position of = in chains from end carbon 1	2	3	4	5	6
395	Fischer Kt. 100 c.c.	200	N_2	200	100					
395	Fischer Kt. 100 c.c.	300	N_2	200	7	45.5	30.1	8.3	5.8	3.0
265	Fischer Kt. 200 c.c.	250	CO	100	3	15.0	20.0	22.0	21.0	18.5
265	20 gm. Cobalt metal	150	CO	100	3	24.0	25.0	18.0	16.0	13.5
265	Fischer Kt. 200 c.c.	150	CO	100	8.1	27.2	23.0	18.1	13.3	10.3
265	65 gm. Iron Pentacarbonyl	150	CO	100	58.2	17.8	8.9	5.7	3.1	4.2
265	20 gm. Nickel Metal	150	CO	75	100					

Heating up in all experiments 1 hour
Held at temperature in all experiments 1 hour

Table on pp. 05647, Reel 14.

The above explanation is necessary to understand fully the importance of the experiments with iron carbonyl as set down in Table I. The conclusions of the German authors in respect to this phase of their experiments were:

7. The fact that iron carbonyl acts to isomerize olefins is of importance in considering the composition and course of this reaction to produce Synol alcohols. Synol alcohol tends to be practically unbranched but the olefins also produced in the Synol process are themselves of branched structure.

It remained to explain the reason for this phenomenon. The German authors thought that in the Synol process alcohols were formed first, after which a dehydrogenation occurred to produce the Synol olefins. These olefins were branched due probably, in view of the teachings of these experiments, to the isomerizing effect of iron carbonyl.

It is important to note that "substantial quantities" of cobalt carbonyl are formed in the first stage of the OXO process. This is dissolved in the reaction mixture, but subsequent hydrogenation "completely destroys' the carbonyl and restores it to the active catalytic condition" (14-524). The continuous process is particularly advantageous in respect to catalyst conservation, therefore.

The aldehydes which are present at the end of the first step of the process can be separated and marketed as such. Indeed, at an early period in the development, production of aldehydes was contemplated from both batch and continuous operations. However, it was found that to react the olefins completely in the first stage, a sufficiently drastic treatment with the water-gas mixture must be employed so that considerable conversion of aldehyde to alcohol is actually obtained in the first stage. The prospect of getting aldehyde as an end product became less attractive to the Germans commercially, as they learned more of the nature of the reaction, including the solution of cobalt compound in the aldehydes just mentioned.

The OXO process is to be looked upon primarily as one for the production of alcohols, and it is not particularly suited to the production of aldehydes. In fact, definite statements were made in interview that when aldehydes were desired, it was probably better to produce the alcohol by the OXO process, then isolate same and use known methods to oxidize it back to the wanted aldehyde.

G. PROPERTIES OF OXO PRODUCTS

The main interest in Germany in the OXO process from the commercial standpoint during the years of 1940 onwards was apparently for the production of wetting and washing agents, obtainable by sulphonating alcohol. It was concluded rather early in the development that the mixture constituting OXO alcohols was better than any of the individual alcohols when converted to washing and wetting agents. Further, that the products were better than the small fraction of similar-number-carbon atom alcohols which could be obtained from the Synol process. Nevertheless, the files contained many comparisons, from one standpoint or another, of the OXO alcohols and the Synol alcohols for washing powder purposes.

Typical of the experimental work done upon the OXO products from the standpoint of their suitability for wetting and washing agents is the discussion contained in a letter from I.G. Farben to I.G. Wolfen (14-659, October 12, 1942). Extracts of this letter are given here to indicate the type of product made by OXO process. Samples of OXO sulfates were being sent to the I.G. Wolfen with a request for their examination, and enlisting their aid in having the samples further tested by others. To explain the nature of the samples, the following information was given in the letter. The samples were of washing powder made of OXO alcohols in the range from C_{12} to C_{18}. The nature of the OXO alcohols before sulfonation is shown in the table below:

OXO Alcohols

	For OXO I Sulfate (C_{12}-C_{18})	For OXO II Sulfate (C_{13}-C_{18})	For OXO III Sulfate (C_{14}-C_{18})
Density at 20°C.	0.801	0.800	0.803
OH	145	130	116

The actual composition of the alcohols whose crude inspections are given above was determined as follows:

Composition	Percent		
	I	II	III
C_{12}	24.0	-	-
C_{13}	18.0	24.8	-
C_{14}	15.3	20.0	26.8
C_{15}	13.2	17.4	23.1
C_{16}	11.5	15.1	20.0
C_{17}	9.3	12.3	16.2
C_{18}	7.9	10.4	13.8
	100.0	100.0	100.0

To obtain these alcohol cuts, the following procedure was used:

Low-temperature thermal cracking of paraffingotsch produced olefins having the following boiling ranges (after fractionation).

		Boiling Range	% Olefins
Olefins for Oxosulfate	I	190-305	56.0
" " "	II	210-305	53.0
" " "	III	230-305	49.0

The "Oxierung" of these cuts was carried out at 130°C. and 200 atmospheres water-gas pressure in the presence of F. T. cobalt catalyst made by Ruhrchemie. Reduction of the resulting aldehydes was carried out at 180°C. and 200 atmospheres with hydrogen. These were sulfonated with chlorosulphonic acid "in the ordinary way". Methanol and sodium hydroxide were added to separate the unsulphonated paraffins and other unreacted materials. Physical decantation followed by benzine extraction was employed to discard the unreacted materials. The purified solution of "soaps" in methyl alcohol so obtained was then evaporated and mixed with sodium sulfate, after which the mixture was dried on a drum drier.

The tests on the OXO products obtained by the procedure first described using the raw materials originating as just indicated, were as follows:

Properties and Appearance of Oxosulfates I, II, and III

The resulting oxosulfates were all fine white powders forming colorless and clear solutions when 5% was dissolved in water at room temperature. Since the solution was slightly alkaline to lachmus, a few drops of sulfuric acid were added to the "stock solution".

Stability in Storage

All of the products took up very little water and remained free-flowing powders, when stored for one week at 20°C. and 65% relative humidity. This was deemed satisfactory.

Wetability

All samples were stated to be excellent, though the figures given are not understood, since the test is not described.

Foaming Properties

Foam volume, when tested by a liter graduate and sieve plate holding the solution at 35°C., was described as good as "Ludwigshafen 387" or "LU 387" and better than "Sekurit", two powders in the market.

Washing Properties

When tested upon both cotton and wool which had been artificially soiled with natural dirt under various specified conditions, the conclusions were that the oxosulfates were substantially as good as the standard "LU 387" or "Sekurit". In a general summary of the properties of the oxosulfates so obtained, the following was stated:

Oxosulfates met requirements of storage stability, wetting power and foam propensity. They are very good both for wool and cotton washing, including "fine washing". It is further concluded that the products should have some of the C_{12} alcohols, i.e., sulfates with it, since the cleaning properties of the powders with wool or cotton are thereby enhanced.

Plasticizers - Esters

Aside from washing powders, the OXO process was used or planned for use by Germans to make phthalic acid ester of alcohols of 7-10 carbon atoms which was alleged to be an excellent "plasticizer". A fragmentary reference to the use of OXO alcohols for plasticizer is contained in a letter of September 17, 1942 (14-651). It seems, according to this communication, that beginning in April, 1943, Ruhrbenzin planned to deliver, at a regular rate, 6,000 yearly tons of a Kogsin 1 fraction, cut to include 7 to 10 carbon-atom-molecules and containing at least 35% olefin.

> "This amount will be sent to Leuna and put through the OXO process, including the reduction. Crude products will then go to Schkapou (site of the rubber manufacturing plant owned by I. G. and near Leuna) and will there be esterified by means of the steam conversion process (the so-called azeotrope process), whereby in place of the usual benzol-xyol mixture to drive off the water the heptane-decane mixture would itself serve the same purpose.
>
> "The separated mixture (about 4,000 tons per year) will be taken back to Leuna and should be sent to the motor fuel section of the plant, but this material could be divided between Holten and Leuna. The palatinols (i.e., phthalic acid esters) will be finished up at Schkapou."

Further reference to phthalic ester production will be found in the next section.