

INFORMATION DIVISION TRANSLATION T46-46

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Synthetic Detergents from Products of Carbon Monoxide  
Hydrogenation

Report by Dr. Roelen, Ruhrchemie

The production of detergents from the product of the carbon monoxide hydrogenation is possible in several entirely different methods today. Also, its large scale use is more or less progressing. Six different operation methods are to be considered.

1. The preparation of primary fatty acids, those fatty acids that are formed primarily as by-products of the carbon monoxide hydrogen synthesis.
2. The paraffin oxidation.
3. The sulfonating of primary olefins or cracked olefins.
4. The sulfochlorination of paraffin hydrocarbons.
5. The synthesis of fatty acids from olefins with water gas by way of the OXO synthesis.
6. The synthesis of fatty alcohols from olefins, CO and H<sub>2</sub> by means of the OXO synthesis.

At present the direct sulfonation of synthetic olefins is not used technically, so far as I know. The reasons for this can be found partly in the properties of the product and partly in the difficulties that are connected with this type of sulfonation. Therefore, I do not wish to go into detail about this method of operation.

There exists already extensive publications about the paraffin oxidation and about the sulfochlorination of paraffin hydrocarbons. Therefore, I can limit myself to mentioning these two methods.

But little or nothing has become known about the preparation and processing of the higher primary fatty acids. But in view of the prevailing soap shortage the latter is of great interest in all synthesis plants, particularly since formation of these fatty acids occurs necessarily during alkali purification (of synthesis product.)

It has been shown that for various reasons it is impossible to report a uniform operation method for the production of usable soaps from the purification alkali solutions. First of all the alkalization is carried out in various ways in the various synthesis plants. Some alkalis immediately after condensation, thus a mixture of all molecule sizes is obtained. Therefore, the wash liquid contained undesirable low and the usable high fatty acids. Others wash the various fractions separately after distillative

separation. Thereby the purification liquid of the diesel oil fraction contains such a fatty acid mixture that the separation of undesirable lower acids will not be necessary for detergent purposes. This is the case at Ruhrchemie.

The different way of alkalizing does not only influence the molecular size of the fatty acid mixture but also its quality. The accompanying impurities seem to be considerably better with regard to kind and amount if one alkalizes before distillation. Such acids can be worked up easier than acids from the distillation fractions. Differences in the makeup of the crude fatty acids seem also to be caused by the differences in the methods of the synthesis. But no further details about this have been determined. Also the concentration of the alkali used is not uniform. Some wash with relatively dilute hydroxide and avoid the formation of emulsion (partly on purpose). Others wash in such a manner that an emulsion layer is formed. In this form a soap concentrate can be prepared easily.

The starting material for the preparation of primary fatty acids is formed in various quality. Therefore, various ways of processing are necessary. When this processing is done for the purpose of production of soaps for wash purposes when it consists mainly of two parts.

1. Removal of contaminating by-products.
2. The finishing of the usable detergent.

The finishing can be done according to known and tested methods of the soap industry. No new operation method is necessary here. One could think that something similar would also be valid for the removal of the impurities by using, for instance, the experiences of the paraffin oxidation. But this is not possible without difficulty; partly because the quantities that have to be processed are always limited, partly because of considerable chemical differences, for instance compared with the product of the paraffin oxidation. We have tested all these methods of operation for the production of soaps from OXO fatty acids and we have partly further developed them and have partly worked out some new ones.

I should like to say something about the nature of the impurities. First, there are dissolved or emulsified hydrocarbons the amount of which depends largely on the concentration of the hydroxide and it may be considerable. These hydrocarbons have to be removed because they reduce the washing reaction. These varying amounts of higher alcohols may be contained. These must be removed as far as possible because even small amounts of it in the finished soap causes disagreeable pulling of the skin. Also iron is present which causes red or brown color but otherwise it does not make any trouble. The worst impurities are finally the odor carriers whose nature is not known in detail. They are very disagreeable because they stick stubbornly to the fatty acids during physical and chemical separation and because even traces cause bad odors on the skin or in the laundry.

As is known the processing of the product of the paraffin oxidation occurs mainly by means of fractional distillation. But the fatty acid distillation is technically not simple and requires acid-resistant building material which at present can hardly be procured. The dissolved iron can be removed by distillation but not the disagreeable odor carriers. Therefore, one tries to get along without distillation, which is entirely possible.

Then the lecturer discussed the most important method for processing of primary fatty acids using a diagram scheme.

Today we have a further possibility for preparing detergents from primary products and carbon monoxide hydrogenation. We used a new reaction that we discovered in the year 1938. It consists in the addition of water gas to olefinic double bonds whereby the next higher aldehydes are formed at first. With suitable conditions also two molecules of the olefin that take part in the reaction can unite with one molecule of carbon monoxide. Thus, also ketones may be formed in this reaction. Thus, it is a generally usable method for preparation of OXO compounds.

For instance, one can obtain propyl aldehyde or diethyl ketone from ethylene; from cyclohexane one can obtain hexahydrobenzaldehyde, from oleic acids oxomethylstearic acid, etc. The reaction conditions are relatively mild, with a pressure of above 50 atms., 100-200°C and presence of catalysts.

In the production of detergents one starts out with olefins of the molecular size C<sub>11</sub>-C<sub>18</sub>, that is, from primary or cracked olefins of the diesel oil region. From this one produces the appropriate fatty aldehydes by means of the OXO synthesis.

For the preparation of soaps it is now necessary to oxidize the fatty aldehyde in the air and to separate the fatty acid and hydrocarbon from the mixture that is formed, in the known manner and to saponify the fatty acids.

If one hydrogenates the fatty aldehyde with hydrogen instead of oxidizing with air one obtains the corresponding fatty alcohol. It is known this can be carried out easily with aldehydes. The separation of hydrocarbons is done practically in the following manner. The fatty olefins are separated in such narrow cuts by fractional distillation before the OXO synthesis that the hydrocarbons that have not been reacted can be eliminated later from the formed fatty alcohols by simple distillation. This synthesis yields nearly chemically pure fatty alcohols of any molecular size with high yields (with yields of 95%). The fatty alcohols that are formed are exclusively primary alcohols, which is a definite advantage for their further use.

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The fatty alcohols are sulfonated by a known method for production of detergents. They yield a product which is entirely equal to those prepared of natural fatty alcohols. A large scale plant for the production of fatty alcohols from primary olefins of Ruhrchemie is under construction in Holten. It will probably be in operation this year yet.

Starting with the fatty alcohols, one can get to fatty acids in known manner by way of alkali fusion. As is known there are available large scale plants for this reaction in Germany. The OXO synthesis offers the advantage that by the way of fatty alcohols sulfonates or soaps can be produced in one and the same plant upon choice.

/s/ Roelen

Martin

The statements of Roelen are to show how one can utilize with simple means the fatty acid primarily for the attendants particularly now during the war. Particular care must be used in the neutralization of soap solutions to prevent skin diseases. Further it is to be considered that by the preparation of fatty acid the cause of some corrosion may be eliminated. Later we shall report in detail about this fatty acid conservation.

Braune asked whether foaming capacity is a measure for good cleaning action of a soap, and whether there exists differences in principle between the usability of low and high fatty acids. Roelen emphasizes that low fatty acid gives all good foam but are less good cleaning agents. The higher acids in spite of the low foaming gives a particular wash effect. Thies points out that the disagreeable acid odor is considerably depressed by heating the hydroxide to 120-140°C for 12-24 hours. Roelen confirms this and states that the simultaneous aeration at high temperatures (that he tested) is very effective.

Martin asked that a short explanation about the cobalt situation should be accepted. Laube says to this.

The procuring of Kieselguhr and thorium and magnesium has not caused any difficulties at present. But the replacement of cobalt has become almost impossible. Ruhrchemie has been acting as agent for the other plants and took over the procuring of raw materials for the cobalt production. They gave particular attention to cobalt stocks before the war. Simultaneously with construction of the synthesis plant also the Letmate plant was arranged in such a manner that our monthly requirements could be covered. Since the Ruhrchemie could buy the product because of the currency agreement with the government 730 tons was procured in 1939 after difficult discussions. Thereby, one must consider that this amount represents half of the yearly world consumption of cobalt. Since the beginning of the war no additional cobalt could be bought abroad. Also no large amounts were found in Finland, Russia, Belgium and France. The supply of cobalt ores from Africa has also become impossible.

At a meeting in the defense department in November 1942 the cobalt situation of the total German cobalt-using industry was discussed. (In the following two paragraphs there are details about the cobalt situation at that time and it is advised to merge all cobalt reserve and it is hoped to be able to operate all plants until 1944.) The problem of whether the other metals can be substituted for cobalt is being worked on by the various companies.

The iron catalyst, which has been worked out by us, is a substitute for cobalt. But it necessitates a reaction temperature of 50°C higher and a higher gas pressure if one desires to process the synthesis gas with similar yield. It seems possible to convert the pressure synthesis to iron catalyst, but we will only be able to give details about it in a few months after a large oven has been put into operation. By conversion of the pressure synthesis cobalt supply could be maintained for a longer period of time for the normal synthesis. It has not been possible to find a solution for the cobalt problem in the normal synthesis. Our plants must provide for the lengthening of the longevity of the catalyst by adjusting the operation, by watching the gas purification as closely as possible and by installing pre-purification plants using activated carbon. That way the loss can be cut down.

Löpmann reported about the experience of the chemical plant Essen Steinkohle. Gases were purified previously by means of activated carbon and also by a method developed by that plant. By the elimination of resin formers and of part of the organic sulfur compound in the activated carbon purification it was possible to save considerable amount of the purified (catalyst) mass. An increased sulfur purity of the synthesis gases was obtained without increasing the longevity of the catalyst which was already 8 months. According to Löpmann's opinion the operation of the two synthesis stages as it is carried out by the Chemical Works, Essen, Steinkohle is to be held responsible for these long running times and thereby for the reduction of cobalt loss. Löpmann points out again in his report about this method on April 18, 1942 which has been sent to all synthesis plants by way of Ruhrchemie. Martin asks to have a detailed report particularly with regard to new experiences to be sent to the various plants. These should test so far as they can whether the method of Essen, Steinkohle can be carried out in their operations. Löpmann says such a written report will be possible in the future.

Martin, thanks for the interesting reports and discussion.

Translated Oct. 16, 1946 - Rochelle H. Bondy

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