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INFORMATION DIVISION TRANSLATION T46-85

Masche Roel 1, Frames 11-14

I.G. Farbenindustrie Main Laboratory, Ludwigshafen, April 21, 1941

About New Ester Acrylic Acid Esters

Authors: Dr. Arzicalla, Dr. Flickinger

Until now the following acrylic acid esters have acquired technical importance: methyl acrylic acid ester, ethyl acrylic acid ester and normal butyl acrylic acid ester. Of these one produces at present about 310 tonnes for artificial materials per month. The ethyl acrylic ester is the most important one.

Since the polyacrylic acid esters are considered particularly valuable in the artificial material field because of their good film setting capacity, we have taken the task to seek systematically for further usable acrylic acid esters. The polymerization of these is being investigated by Dr. Fikentscher and Dr. Holscher.

At first we prepared acrylic esters azeotropic with the technically-formed 50-60% acrylic acid. But it was found by us that it is much more advantageous to work with the 90-100% acrylic acid which has been prepared by Dr. Fikentscher and Dr. Runkel. Thereby, one obtains better yields of esters in the esterization of less water-soluble alcohols because of better miscibility and shorter reaction time. Also, the processing is much easier because of the elimination of large amounts of polyacrylic acids. The polydecalolvinyl ether showed interesting solubility and furnished particularly hard products. We prepared first the decalolacrylic ester (boiling point 118-122°). It yielded, after polymerization also hard and very soluble products which were considered interesting for various purposes.

The decalylcarbinol prepared by Dr. Schuster by the Oxo synthesis from octaline yielded also hard polymerizates after esterifying. These were still more-soluble in naphtha than is the case with the decalolacrylic ester.

The isobutyl acrylic ester (boiling point 55-60°) did not show till now any particular advantage over the normal butyl acrylic ester.

Also the nonyl alcohol acrylic acid ester (nonyl alcohol from diisobutylene after the Oxo process) showed also very favorable properties. This polymerizate yields a very viscous oil and it may be interesting above all as softener for polyacrylic esters because of its good compatability.

We converted also ethyl hexanol into the acrylic ester (boiling point, 60-68°), since it is yielded as a by-product of the butadiene synthesis. It has similarly interesting properties as the ester of nonyl alcohol.

Nothing can be said at present about the following other mono acrylic acid esters which we have also prepared:

Benzyl acrylic ester, t.p.₄: 100-105°
Cyclohexanol acrylic ester, b.p.₅: 76-79°
Secondary butyl alcohol acrylic ester, b.p.₁₅: 48-53°
Oxy ethyl cyclohexanolic acrylic ester, b.p.₃: 70-110°
Oxy ethyl isopropyl acrylic ester, b.p.₂₀: 40-48°
Tetra oxy ethyl - decalolacrylic ester, b.p.₄: 115-170°
Oxy ethyl beta naphthol acrylic ester, m.p.: 62°
Glycol monomethyl ether acrylic ester, b.p.₁₂: 60-62°
Glycol monobutyl ether acrylic ester, b.p.₂: 85-90°

We prepared another series of acrylic esters which may be considered for fatty components because of the number of their double bonds.

Allyl acrylic acid ester, b.p.: 104-110°
1,4-butenediol diacrylic acid ester, b.p.₂: 97-100°
1,4-butanediol diacrylic acid ester, b.p.₆: 105-110°
Trimethylol propane triacrylic acid ester; cannot be distilled

Because of two reactive double bonds that are distributed on a small molecule in the allyl acrylic acid ester, it yields extremely short and crumbly polymerizates. The butenediol diacrylic ester showed the same properties, while the butanediol diacrylic ester was evaluated more favorably as usable wetting components.

The trimethylol propane triacrylic ester polymerizes very well and yields extremely hard polymerizates. But these are insoluble in all solvents because of the extreme wetting. Therefore, the ester can only be considered for mixture polymerization and molding polymerization.

Further, we have prepared interesting diacrylic acid esters from polyethylene oxide which are water soluble in the monomeric form similarly to the divinyl ether. They are easily polymerized also in aqueous solution with hydrogen peroxide or persulfates into insoluble strongly swelling products which give up their water in drying and form brittle (friable) substances. If one uses in the esterification methyl polyglycol with longer ethylene oxide residues (for instance 10-60 molecules), one can prepare polymerizates which are water-soluble and which can be diluted with H₂O up to a certain degree. They could possibly be used as thickening agent or for textile purposes.

SUMMARY

This is a report about new monomeric acrylic acid esters whose polymerizates are still being tested.

/s/ Flickinger and Krzikalla

Translated - Oct. 31, 1946 - Rochelle H. Bondy
Checked - Nov. 15, GCM

INFORMATION DIVISION TRANSLATION T46-77

Hasche Reel 1, Frames 15-17

I.G. Farbenindustrie Main Lab., Ludwigshafen, April 21, 1941

About New Vinyl Ether II.

Authors: Dr. Krzikalla, Dr. Flickinger

In our last Zetko report of April 24, 1940 we listed new vinyl ethers. Of these only decalolvinyl ether is used much in the form of pure or mixed block polymerizates. At present 10-20 tonnes per month are manufactured and it will probably be soon increased by a further 10 tonnes per month.

The total manufacturing of vinyl ether was increased within the last year from about 210 tonnes per month to 300-320 tonnes per month. This is distributed to 7 vinyl ethers altogether.

In the meanwhile a number of new vinyl ethers have been prepared, for which we use partly new incidentally formed alcohols, and partly also compounds which have been chosen for special reasons. These shall be named briefly in the following. At present they are being tested in detail for polymerization by Dr. Fikentscher and Dr. Holscher.

Vinyl ethers of aliphatic and cycloaliphatic alcohols

Nonyl alcohol vinyl ether, b.p.₁₂: 72-75°C

Ethyl hexanol vinyl ether, b.p.₁₁: 61-63°C

Vinyl ether of the alcohol from Michael synthesis naphtha,
b.p.₁₅: 35-55°C

Decalyl carbinol vinyl ether, b.p.₁₄: 115-122°C

Of these vinyl ethers those made from nonylalcohol, from decalyl carbinol and from the alcohol from the Michael synthesis naphtha are of special interest. These alcohols may possibly be prepared on a commercially favorable basis. These three alcohols were obtained after the Oxo process from olefins with carbon monoxide and hydrogen by Dr. Schuster and Dr. Eilbracht.

The nonyl alcohol can be easily prepared from the commercially available diisobutylene, the decalylcarbinol is prepared from octylene, and the alcohol from the Michael synthesis naphtha from the corresponding naphtha (compare report of Dr. Schuster in the same Zetko report).

Ethyl hexanol is formed as a by-product of the butadiene synthesis in the 1.3 process and in the 1.4 process. It represents a favorable basis for the preparation of vinyl ether. The first three vinyl ethers that are mentioned above are much branched and may be of particular interest for this reason. According to experience polymerization products of vinyl ether from branched alcohols are harder than those from corresponding straight chain alcohols. For this reason, also the polymerization product of vinyl ether from secondary and tertiary alcohols may be interesting. Of these the following has been prepared so far:

Secondary butyl alcohol vinyl ether, b.p.₅₅: 30-35°

Methylphenyl carbinol vinyl ether, b.p.₁₄: 70-73°

Cyclohexyl methyl carbinol vinyl ether, b.p._{15r}: 68-69°

The following are still being worked on:

Naphthyl methyl carbinol vinyl ether

Isopropyl methyl carbinol vinyl ether

Trimethyl carbinol vinyl ether

Triphenyl carbinol vinyl ether

In general, it can be said that secondary and tertiary alcohols are somewhat harder to vinylate. Therefore, the preparation conditions have to be tried for each case. Further the following vinyl ethers were prepared:

Butyl cyclohexanol vinyl ether, b.p.₂: 80-90°

Diox-ethylresorcindivinyl ether, b.p.₅: 215-225°

Pentox-ethylphenol vinyl ether, b.p.₆: 190-240°

Tetraox-ethyl decalol vinyl ether, b.p.₆: 160-220°

The larger boiling intervals in the last two vinyl ethers can be explained by the fact that in the oxo-ethylation one never obtains a uniform product but always a mixing of lower and higher oxyethylated products.

We also vinylated polyether oxides, for example, P₁₀, P₂₀, into divinyl ethers. These vinyl ethers are water-soluble but they are unfortunately not easily distilled and cannot be crystallized so that their pure preparation which is important for later polymerization causes first difficulties. In polymerization these products become water-insoluble

which may make them promising for textile purposes. Further we have obtained water soluble monovinyl ethers through addition of longer ethyl oxide residues to monovalent alcohols, for instance to methyl alcohol, and through following vinylization. These monovinyl ethers cause similar difficulties in purification of the divinyl ethers. They yield soluble polymerizates. More work will be done about all these vinyl ethers.

Vinyl ethers from heterocyclic alcohols

The following vinyl ethers were prepared from heterocyclic alcohols:

Tetrahydrofurfuralcohol vinyl ether, b.p.₁₈: 58-64°

Oxytetrahydrofurane vinyl ether, b.p.₁₅: 46-48°

n-beta oxyethyl pyrrolidon vinyl ether, b.p.₃: 125-135°

Particularly the heterocycles which contains oxygen in the ring are interesting, because of their favorable solubility properties since their polymerizates have very desirable compatibility with many artificial materials.

The tetrahydrofurfural alcohol can be easily obtained through hydrogenation from furfural. The oxytetrahydrofurane can be obtained easily from trioxybutanes by way of butindiol. Thus they both have favorable material foundations. The vinyl ether of the oxytetrahydrofurane is difficult to dissolve in water, while the polymerizate is water-soluble. It has the same properties as the polymethyl vinyl ether, namely, it is insoluble in hot water.

Summary

This is a report about further newly prepared vinyl ethers from aliphatic cycloaliphatic and heterocyclic alcohols.

/s/ Flickinger and Krzikalla

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Checked Nov. 15, 1946 - GCM

INFORMATION DIVISION TRANSLATION T46-83

Hasche Reel 1, Frames 221-230

Höchst Plant, April 1941, Scientific Zetko Exchange 1941

I. G. Farbenindustrie

About: New Use Possibilities for Anthracene

April 23, 1941

Author: Kränzlein

The four year plan ordered by the Führer at the end of 1936 first of all brought Chemistry the especial obligations not only in the direction of an autonomous large scale technique, but also new problems in the foreground of interest and research. The office for German raw and industrial material, or the Reichsamt for economic development proceeding therefrom, have from 1937 till now carried on with especial emphasis in a cooperative work substitute "resin-free paper sizing" for colophony, which in the old Reich was used in an amount of about 25,000 tonnes per year. Encouraging the accomplishment of the Four Year Plan, there participated in this cooperative work several chemical professional colleagues of the office, university professors, men from the paper industry, and several experts of German industries basied in the sphere of synthesis of resins and high polymers.

The first meeting on the project occurred on November 12, 1937. The difficulty of the problem of finding a cheap usable substitute for colophony seemed insurmountable to many present. Regarding the possibility to bring paper into commerce only unsufficiently sized, or un-sized, it could be used only in a few cases. Therefore the first line prospect of an especially intensive use of the resins of the German forests was discussed:

- (a) by the labor service,
- (b) following Professor Hessenland's stimulation (irritation?) process. Regarding this, Prof. Hessenland was indeed paid a monetary consideration through the I. G. but declined a transfer of his domestic and foreign patents.
- (c) An extensive recovery of colophony by extraction of comminuted spruce wood, after the process recommended by Dr. Asser in the manner which can be followed.

It was clear that the colophony basis for the sizing of paper will remain continually very slender. In consequence of this, the adulteration possibilities of colophony were discussed a) by montan wax, b) by water-soluble cellulose derivatives, c) by phenol resins, whose instability toward light was immediately objected to. The addition of a) or b) to colophony sizing can be done only in certain limits, because they give the sized paper a different and insufficiently pliable character.

It is recalled for comparison that in the adhesive industry many thousand tonnes of grain are spared through advantageous substitution of the gluten contained therein by 1200 tonnes cellulose in the form of Tylose.

Ludwigshafen in its Luresin-Marken, the condensation product of ammonium sulfate formaldehyde and acetaldehyde, has achieved a very remarkable progress in the search to find a suitable extender for colophony for the paper sizing. This achieved a 50% extending and large sales of its resin extender, which came at the right time. In between, other firms beside the I. G. have offered new extender products, for example the followers of the Mitcherlich Cellulose chemists. These extenders lost their original importance in that colophony was offered even less on the market.

It was therefore especially of value to produce a fully synthetic paper sizing instead of the colophony. In following out this pressing problem, the limits are drawn very narrow, for starting materials must be chosen which are available in large amounts and sufficiently cheap. First, one starts with crude anthracene. It is a mixture of three-ring systems, and indeed next to anthracene and phenanthrene constitution seems to be a suitable basis for a substitute for abietic acid. (1)

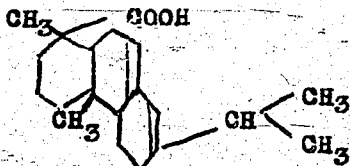
Also the use of anthracene has been decreased considerably thru the competition of naphthol as dye and other azo dyes. Previously it has been prepared in considerable amounts from crude anthracene for alizarine and other important dyes of the anthrachinone series. The available separation and purification plants for crude anthracene are therefore not being used by the I. G.

Truly one uses crude anthracene again as valuable, but poorly-yielding utilized crude materials of technical manufacture of lamp black for Buna. Thus, the crude anthracene as starting material is now quite short. But the lamp black manufacture can be directed into other channels which is very probable. One found the Nirosons (tetrahydrocarbazol) as Vinyard damage combatting agent in recent years, which shifted the conditions in the crude anthracene field entirely. Previously carbazol and phenanthrene were the waste products of the anthracene purification. But it will soon be the anthracene-phenanthrene mixture will be formed in the future preparation of carbazol from the crude anthracene. Naturally, these will be considerable amounts which will be formed more expensively in their enriched state than a crude anthracene. The anthracene-phenanthrene mixture, which has been freed of carbazol and has been concentrated, is formed in a ratio of at least 3:1 to carbazol, and must be burdened with a considerable portion of the separation costs in order to make carbazol cheaper. Therefore, it would be too expensive for the lamp black preparation. Therefore, it must be the goal to use the two waste components by chemical synthesis for a different purpose.

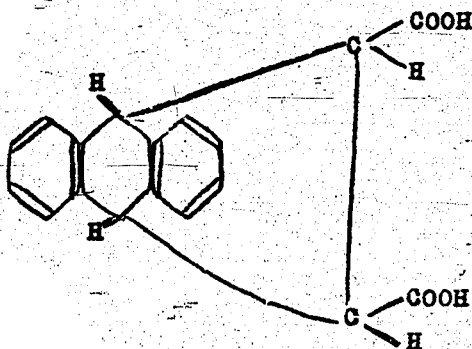
(1) We would not want to miss in our investigations the three ring system of the carbazol and its derivatives. We shall investigate the carbazol, the n-alkyl carbazol, and the tetrahydrocarbazol which is prepared from cyclohexanon or its derivatives and phenylhydrazine.

In the minutes of the discussion about "Resinless paper sizing" on April 4, 1938, at the government agency for economic development in Berlin the following has been noted: "Dr. Kränzlein of I.G. Farben reports about interesting experiments which are in progress at present to build up new artificial resin combinations which are to be suitable especially for purposes of the paper sizing. The constitution of abietic acid is the basis for these synthetic investigations. He is striving for products which approach in their properties abietic acid as close as possible. This synthesis goes out from crude anthracene, therefore, one has reason to expect that these products can be produced at economically tolerable prices. These investigations are still in progress and nothing further can be said about them at present". I shall point out that the investigation direction which has been indicated has been granted priority. Thereby undisturbed progress of the work was assured. Thus, new products could be synthesized which are valuable substitute products for the colophony

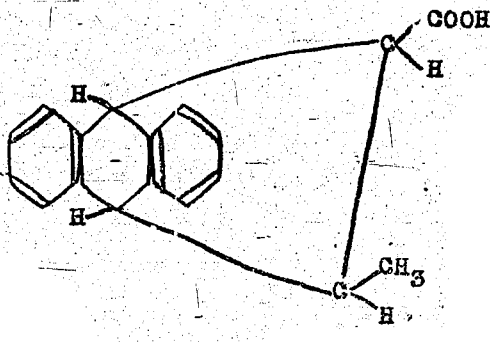
Many were of the opinion that the substitute paper sizing substituting for colophony would have to show similar thermoplastic properties as for instance the aluminum abietate must show in the hot calender. In the synthesis of a resin sizing one was concerned in the beginning particularly to approach the chemical constitution of abietic acid of colophony as closely as possible. According to Ruzicka the constitution of abietic acid of the colophony is as follows.



Thus, it is a carboxylic acid of a hydrogenated 3 nuclear system with alkyl or endo alkyl fragments. In order to attain something similar, anthracene was converted with maleic acid anhydride or crotonic acid into the following addition products:



I

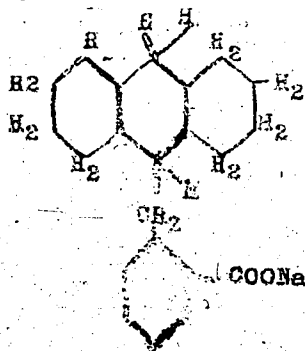
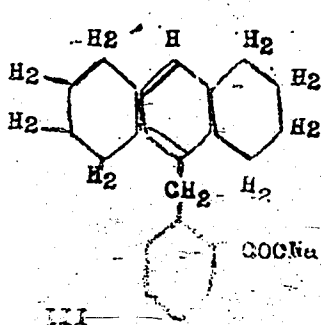


II

It was already to be considered in its properties for paper sizing but not sufficient. One must be grateful to Dr. Wolfram for recognizing the much better properties of the crotonic acid-anthracene addition products (III) compared with the addition product #I. This crotonic acid-anthracene addition product forms the basic carrier of the glue in the paper size A, B, and C which is being sold. Strangely the advantages of this addition product have only about a third of the sizing action of the colophony. No improvement could be obtained thru catalytic hydrogenation of the addition product.

Thus, one had to search for a better basis of the three-ring hydrocarbon.

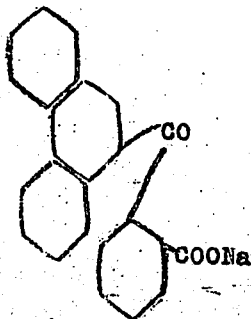
The following products were prepared in following the considerations to this point, to approach the constitution of the abietic acid:



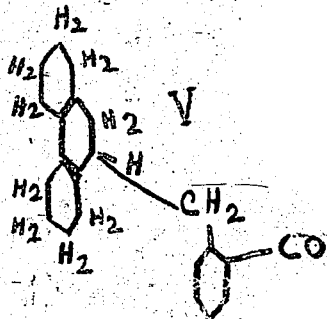
This product was recognized as particularly valuable for the paper sizing. It is the expected and desired 3 system of benzol fragments, it is hydrogenated, it has a carboxyl group and it has an endo-alkyl fragment. Thru this systematic copying of a constitution of the abietic acid one showed again that it is particularly the chemical constitution of a natural product which yields the desired effect, while the arrangement and changing of molecular configuration is not important. This result shows that one can use a linear three ring system as it is present in the anthracene to attain a sizing effect which is at least as good as that of the abietic acid of the colophony in which the 3 ring system is arranged angularly. This seems particularly surprising since the new synthetic resin glue substance, which apparently is a mixture of the formulas 3 and 4, melts in pure state at 225°, and in technical state at 205-210°. The physical behavior of the synthetic anthracene derivative cannot be compared with that of colophony. The new paper sizing does not have the property of a resin milk which is prepared from the colophony with a considerable excess of alkali in form of about a 30% dispersion and so brought into commerce. The new paper gluing agent is the 100% dry sodium salt of a mixture of the formulas III and IV. It offers a large saving in freight shipping. It is much superior in simplicity of use thru simply spraying it into the paper suspension as well as its greaser productivity as compared with the old colophony dispersion.

The products according to formula III and IV are prepared by condensing anthracone with phthalic acid anhydride according to the Friedel-Crafts method. And the sodium salt of the so-obtained 9-anthraceneoyl - o-benzoic acid is catalytically hydrogenated. It is preferable to start from the octahydroanthracene because one obtains better yields in the condensation with phthalic acid anhydride. Also the sodium salt of the octahydroanthraceneoyl-ortho-benzoic acid is more stable in the catalytic reduction. It is not inclined to splitting off the phthaloyl fragment which occurs in the hydrogenation of the sodium salt of the 9-anthraceneoyl ortho benzoic acid.

It was still tried to condense octo hydroanthracene directly with pthalide, in order to save aluminum chloride and make the preparation cheaper. The condensation product of phenanthrene with phthalic acid anhydride, the 9-phenanthreneoyl-ortho-benzoic acid has the following constitution:



So far this has given dihydrophenanthreneoyl-benzyl-ortho-carboxylic acid in the hydrogenation of the sodium salt in aqueous alkaline solution, which did not approach the gluing effect of the hydrogenated anthracene derivatives III and IV. For this reason one prepared also octahydrophenanthrene from the phenanthrene, and condensed with phthalic acid anhydride. This product had almost no gluing action. Therefore, one hydrogenated further in order to convert the carbonyl group into a methylene group. This phenanthrene derivative with the following constitution:



If one could prove that this phenanthrene derivative of this constitution has also a good sizing effect, then one would have a particularly good hope to get good results in the investigations which are in progress. One reaches that way a separation method of the crude anthracene which could be worked out without solvent. The processing of the crude anthracene would be done in such a manner that the carbazol in the crude anthracene would be converted by corresponding amount of potash into carbazol potassium and anthracene-phenanthrene mixture. The carbazol potassium can be eliminated as lower layer from the fusion, and directly hydrolyzed by water into the carbazol and potassium hydroxide. This has been done already in large scale experiments at Höchst. The carbazol can be used without further processing for nitration, and the potash is evaporated and ignited, and then used for solution of the anthracenoyl-ortho-benzoic acid which is to be hydrogenated. Thus nothing is lost from the separation medium. The molten anthracene-phenanthrene mixture which remained in the kettle can be distilled out in light color from a column with intermediate dephlegmators. If one can prove that the hydrogenated phenanthrene derivative which has been described in formula V is also suitable for the paper sizing then one has made available for a valuable use an excellent starting mixture which is formed in large amounts. It is possible that a accumulating action of the anthracene and phenanthrene derivatives of the formulas III, IV, and V will be present in the paper sizing.

We shall continue our investigations and the next time we shall be ready to make more detailed statements about the cost price and the existing practical results in the experimental scale.

The phthalic acid anhydride condensation with anthracene, respectively, phenanthrene, or its hydrogenation products by getting optimum yields has been prepared by Dr. Langbein. Number I¹ and the hydrogenation product has been prepared in known expertness by Dr. Schlichenmaier. These men either made or cooperated in the announcements in this new field.

/s/ Kränzlein

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Trans. Nov. 5, 1946, Rochelle H. Bondy
Checked Dec. 5, 1946, C. C. Miller

Hasehe Reel 1, Frame 338-339

I.G. Farbenindustrie, Frankfurt A.M.

Exchange of Scientific Investigations in the Zetko Field in May 1941

The Influencing of Isomer formation in the Dichlorination of Metaxylo

The chlorination of metaxylo into a mixture of 2,4 and 4,6 dichlorometaxylo has been described already in the literature. No concrete number exists about the quantitative ratio of the various isomers in the mixture. Also the indications about the 2,4 dichlorometaxylo seems uncertain. Detailed investigation shows now that the dichlorination of the metaxylo in the presence of the usual chlorine transfer agents, particularly by the use of sublimed iron chloride, there is formed an isomer mixture which solidifies at about $+17^{\circ}\text{C}$, after fractionation in vacuum in a column. The various isomers cannot be obtained in pure form through fractional distillation. Their boiling points lie too close together. There only occurs the separation of monochloroxylo that are formed, and of the superchlorinated portion. The solidifying point of 17° indicates on the solidifying point curve that the isomer mixture contains about 65% 2,4 dichloro and 35% 4,6 dichloroxylo. It can be separated almost quantitatively according to the method which we applied for in a patent. It consists of a selective sulfurization (sulfonation?) which is described in the report "Process for the Separation of 2,4 and 4,6 dichloroxylo".

In further chlorination investigations of the meta xylo the method of reaction of a series of mixed catalyst was tested. It was found that the use of antimony trisulfide as a chlorine carrier may cause a fundamental shift of the isomer mixture. If meta xylo is chlorinated in the cold in presence of antimony sulfide, one obtains an isomer mixture of a solidifying point of about 41° . This is after the monochloroxylo and super-chlorinated portions had been separated in a column under vacuum. The isomers are divided in the mixture reversely according to their solidifying point curve. About 40% of 2,4 dichloro- and 60% of 4,6 dichlorometaxylo were formed. The separation of this mixture can be carried out easily according to the method that was mentioned before. It was necessary to obtain the isomers in pure form in order to determine the quantitative amount of the various isomers. The physical data for 4,6 dichlorometaxylo seems convincing according to indications in literature and could be confirmed. Those for the 2,4 dichlorometaxylo seemed improbable and could not be confirmed. The preparation of the pure 2,4 dichlorometaxylo was done in the following manner. The acetyl compound of the symmetric meta xylo was dichlorinated. After saponification of the dichloroacet-compound one obtains dichloro xylo. This melts at $74-75^{\circ}$ after repeated redissolving in changed solvents. The 1,3 dimethyl 2,4 dichloro 5 amido benzol was obtained, which yielded a 2,4 dichlorometaxylo of a solidifying point of $4,9^{\circ}\text{C}$ after the entamidation. According to indications in the literature, 2,4 dichlorometaxylo is supposed to solidify at -20°C .

These investigations were applied for in a patent.

/s/ Engelberg II

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Checked Dec. 5, 1946 - CGM

INFORMATION DIVISION TRANSLATION T46-87

Hasche Reel 1, Frames 477-493

I.G. Farbenindustrie, Uerdingen Plant

Scientific Zetko Exchange 1941

Report About: The Catalytic Oxidation with Atmospheric Oxygen in Liquid Phase

I. The Oxidation of Ethylbenzol to Acetophenone. (Dr. Pinkernalle, Dr. Kroning)
April 30, 1941

The catalytic reduction in liquid phase has been successfully used in various ways in the technique. But the corresponding reaction, the catalytic oxidation in liquid phase was technically used only in few cases. The acetaldehyde oxidation to acetic acid or acetic anhydride, and the analogous oxidation of croton- or cinnamic-aldehyde to the corresponding acids are such cases. Also the paraffin oxidation which has been studied much recently should also be mentioned here.

The catalytic oxidation in the vapor phase (because of the relatively high temperatures that have until now been necessary) was successful only when the end products were very resistant to further oxidation. This was the case for phthalic acid anhydride, for anthraquinone and somewhat less for maleic acid. But the catalytic oxidation in liquid phase (because of the considerably lower reaction temperatures) offers much greater opportunity for carrying out partial oxidation of organic compounds. Both of these methods have the advantage of using the cheapest oxidizing agent, oxygen of the air, which, in addition, has the advantage of forming only water as by-product.

Based on this knowledge the catalytic oxidation in liquid phase has been studied for sometime at Uerdingen. The results of the investigations of Dr. Binapfl and Dr. Krey are to be pointed out especially. These investigations (so far as they were put into writing in German applications, patents and Zetko reports) are summarized in Appendix I at the end of this report. Hydrocarbons like paraffins, cycloparaffins, aromatics, alkylaromatics and hydroaromatics, and also aromatic (hydroxy-compounds like phenol, cresol, β -naphthol, benzylalcohol, etc., were investigated.

The experiments on the oxidation in liquid phase of ethylbenzol to acetophenone which are to be described here, were progressing well even upon transferring them to a technical scale. This motivated Dr. Mittag in Uerdingen to take up again the studies about oxidation in liquid phase by means of oxygen or oxygen containing materials on a broader scope. This led to the gratifying results that are described in the reports that follow this one.

1. The oxidation of ethylbenzol with air

As can be seen in Appendix I the investigations about air oxidation of ethylbenzol at Uerdingen led already in 1936 to German Reich Patent (DRP)

522255. It was found then that alkyl benzol can be oxidized easily at 100° with addition of 1% cupric oxide as catalyst by blowing in air. But the reaction stops after about 30% of the charged ethylbenzol is oxidized. The rest remains unchanged. Thus the catalyst loses its effectiveness after a conversion of 30%. Also an addition of fresh catalyst does not start the reaction again (Zetko report of Dec. 15, 1927). The oxidation product is about 30% acetophenon and the other 20% is mostly phenyl-methyl carbinol, also some benzoic acid and a small tar-like residue.

As is to be seen from Zetko report of May 2, 1933, the oxidation product which consists of acetophenon and phenol methyl carbinol was oxidized to pure acetophenon in a few experiments with potassium bichromate and sulfuric acid. A much lower cost price was calculated than that for the old preparation method from benzol, acetylchloride and aluminum chloride.

The acetophenon that was prepared only on a small scale acquired more interest later; thus the oxidation of ethylbenzol was studied again.

The most favorable experiment carried out in 1936 ran approximately as follows.

In two vertical 12 l. iron pipes in series which could be heated from the outside with steam 20.8 kg ethylbenzol was oxidized by blowing in air. The catalyst was 300 g freshly precipitated dry copper oxide. The reaction towers are each provided with a reflux cooler which carries a water trap in order to take the water out of the reaction immediately after its formation. After about 50 hours, after about 6500 l. air were blown through, the oxygen content of the waste gas rose quickly from 0.2% to 20%. The reaction stops then. The catalyst was filtered off and the filtrate was divided by fractional distillation under vacuum.

Thereby was obtained:

13.757 kg.	recovered ethylbenzol (thus 7.046 kg have been used)
6.210 "	crude ketone (consists of about 80% acetophenon and about 20% phenyl methyl carbinol)
0.132 "	benzoic acid
0.361 "	tar
20.460 "	obtained
0.343 "	Loss in operation (not considering the oxygen take-up)
20.803 "	charge

In the previous experiments the following factors were troublesome, the fact that the catalyst cannot be used more than once (therefore, its poisoning) the relatively long reaction time, and the fact that the conversion only is 30%. Besides one had to try for a more favorable ratio of ketone: carbinol in favor of ketone in the production of acetophenon. When the experiments were taken up again the main goal was to eliminate these four disadvantages as much as possible.

In the first new experiment on a half-technical scale an apparatus (Plant II Frame #157) was used which consists of a shell tube which was put together from two long drum tubes R1 and R2 which are about two meters long and 130 mm wide inside. They are joined with a connection piece which is provided with an opening for a thermometer. The pipes had separate heating casing which can also be made into cooling jacket and a liquid circulation tube FU which can be opened or shut as desired. The lower tube is provided with an inlet valve A1 and a gas introduction pipe E. The upper part is closed up with a reflux cooler K, which has a water trap WA. The waste gases (N_2) pass through a gas meter and reach the outside from there. A branching valve A2 makes it possible to undertake gas analysis with an Orsat apparatus, to determine the oxygen content of the waste gas from time to time. The reaction pipe is filled by a pump and is emptied through an outlet valve A1.

A series of charges of each 100 kg. ethylbenzol were oxidized in this experimental apparatus, the following was determined.

- A. The residence time yield was about 8 grams per liter, and hour.
- B. The circulation through the side pass could be shut off without considerable influence on the course of the reaction.
- C. The charges run regularly within 24 to 30 hours until a conversion of about 30%, when fresh copper oxide catalyst was used. After that the reaction stops, the oxygen absorption and the water formation has stopped also.
- D. The copper oxide that was recovered through centrifuging or filtering off proved to be ineffective also for the next charge with fresh ethylbenzol. In fact, a charge that had been prepared with used catalyst could hardly be brought to absorb oxygen even after addition of fresh copper oxide.

Further experiments, carried out partly in the laboratory and partly in experimental operation, showed that used catalyst can be reactivated through various treatments such as blowing out with steam, drying and grinding, or stirring up with dilute sodium hydroxide and washing with water. Admixtures of the basic or acid agents to the catalyst or to the total charge, like MgO , BaO , Ag_2O , organic bases, benzoic acid, acetic acid, acetic acid anhydride, showed in many cases an impairing influence, but did not bring noteworthy progress in any case.

In the meanwhile we started to operate a shaft tube of about 4.5 meters length and 30 cm. inside width, with a total volume of about 320 liters which could be filled in operation with 250 kg. For safety reasons the pipe was closed above with a cover of 5 mm of sheet lead. First the charges ran like described above, whereby the catalyst amount was reduced from 1% to 0.05% gradually. After about 30 charges had been run in the pipe a violent explosion occurred in the operation of a charge. The lead safety cover was torn open and the greater part of the reaction material was thrown out of the pipe. The peroxide determination which was undertaken afterwards showed still a content of 0.13 g. of O_2 which equals 0.56 g. of ethylbenzol peroxide in 100 cc. of

oxidation liquid. In this experiment which exploded after 4 hour running time, the oxygen of the waste gas was 0.2 to 0.3% in the first hour, the water that split off per hour amounted only to 100 cc, while it normally was between 500 and 600 cc. Thus a great accumulation of peroxide must have taken place.

It is known from other oxidation processes that dissolved heavy metal salts require care for a similar peroxide decomposition. In order not to introduce foreign metal and a foreign acid in the process, we decided to add small amounts of copper benzoate to the copper oxide. Such a catalyzing mixture actually causes regular oxidation. Therefore, no peroxide accumulations were observed again, either in the laboratory or in the half-technical scale experiments. (320 liter tube). We determined the peroxide content repeatedly in the oxidation liquid according to the ferro-thiocyanate method. We always found values between 0.05 and 0.07 g. O₂ in 100 cc. We ran one experiment on purpose with copper oxide alone. The experiments (270 kg.) ran for 5 hours and yielded only 250 cc. of reaction water. Then we added 25 g. of copper benzoate and immediately a violent water splitting occurred which amounted to 1,400 cc. in the next hour. The following hours show a normal formation of 500-600 cc. Here an accumulation of peroxide had taken place, which decomposes normally upon addition of copper benzoate. By the use of this catalyst mixture a safe technical operation was assured.

The problem of the increased reaction had to be found yet. The experiment carried out without result with copper oxide and copper oxide-copper benzoate urged us on to try other catalysts particularly other metals for their effectiveness. In our German patent 522,255 one describes besides copper oxide, also the oxide, hydroxide and salts of iron, manganese, cobalt and silver as suitable. Yellow iron oxide is somewhat catalytic in the air oxidation of ethylbenzol but the oxidation runs lower than with copper catalyst.

At the Huls plant one found at that time that considerable reaction increase could be obtained when the heavy metal soligen* was used as catalyst, which are known from the Oppau paraffin oxidation. A lead-manganese-cobalt-soligen is supposed to be particularly effective. Further experiments shows us, somewhat later than in Huls, independent from one another, that cobalt was the most effective catalyst metal. It is practical to use such compounds which are soluble in organic solvents, as salts of organic acids (naphthenate, palmitate) but also as more difficultly soluble compounds such as benzoate, a cetyl acetate and phthalocyanine.

*Translator: "Solagen" is defined in H.A. Curtis' Glossary - PB #475 - as "A dryer for oils. The manganese or cobalt salts of higher fatty acids from the Fischer Tropsch "Kogasin".

by the solubility in 10-85% sulfuric acid. Pure acetophenone dissolves in it with light yellow color and it is clear. Traces of carbinol cause more or less turbidity. In Appendix III a series of mixture solidifying points and the corresponding solubilities in 30% sulfuric acid are summarized. In this table one can see that the carbinol content can be determined exactly on basis of the solidifying point. The following paragraphs deal with various processes which we have worked out for the preparation of pure acetophenone.

The following have to be considered here:

The oxidation of the ketone-carbinol mixture in such a manner that only carbinol is oxidized into ketone.

The separation of ketone and carbinol is done by fractional distillation, by fractional crystallization, by the separation of crystallized ketone complex compounds (oxonium salts).

The separation of the carbinol by converting it into styrol, and adjoining fractional distillation.

In order to decide which process is advantageous economically, the quantitative ratio of ketone to carbinol is of great influence, because larger carbinol amounts cannot find utilization at present. Pure preparation methods were of little interest in the beginning, when we still had 20% of carbinol in our crude ketone. Predominantly we worked on the after-oxidation of the mixture with dichromate. In experiments for catalytic dehydrogenation of the carbinol portion in the mixture by means of air over copper catalysts, we found that carbinol can easily go over into styrol by splitting off water. Since this can easily be separated from ketone through fractional distillation and can be used in any amount, this method was worked through technically.

a. After oxidation with dichromate-sulfuric acid - The oxidation of the carbinol which is contained in the distilled oxidation product to acetophenone (named in the following "A.P.") with dichromate-sulfuric acid was already carried out successfully in Uerdingen in 1926. Therefore, the new investigations were mainly about converting the dichromate oxidation into a technical styrol.

First the method was tested once more in the laboratory and 3 kgs. samples, with solidifying points of 13.05° (3% carbinol), 16.6° (7% carbinol) and 14.8° (12% carbinol), were oxidized. We worked with a 10% dichromate excess and a reaction temperature of 50-60°, a reaction time of 6 hours. The acetophenone which was obtained in the process was always unobjectionable and it had a solidifying point of 19.2 to 19.5°C.

In the following a technical charge is reproduced which was carried out with a distilled oxidation product of a solidifying point 14.8°, thus with a carbinol content of 12%. The following oxidation was carried out in a masoned 12 cu. meter stirring kettle which was connected with a reflux cooler, a rising tube, thermometer pockets, and supply vessel.

4,618 tonnes of ketone-carbinol mixture with a content of 554 kgs. of carbinol.

0.429 tonnes of sodium dichromate
0.614 tonnes of concentrated sulfuric acid
1.94 tonnes of water

reaction temperature 50-60°C

reaction time: 7 hours running in of the oxidation liquid, and 14 hours of stirring.

After the chrome liquor is let out, the crude oil is washed with water. The chromate liquids still contain 40.8 kgs. of sodium dichromate. The crude oil is washed again with water and finally it is distilled in vacuum. 4.636 tonnes of crude product were sucked into the retort (still contained some water).

1. Pre-cut water content A.P. with little ethylbenzol and styrol 368 kgs. = 7.76%.

2. Main fraction (A.P.m.p. 19.2-19.4°) 3,889 kgs. = 84.2%.

3. After-cut (A.P. with 2% carbinol m.p. 13.5°, 187 kgs. 4.05%).

4. Residue 131 kgs. = 3.9%. That adds to 4,615 kgs. which equals 99.91%. Distillation loss 21 kgs., distillation time, 40 hours.

An examination of the pre-cut shows this consists of at least 70% pure A.P. It was necessary to rinse the run-off absolutely water free so that about 90% pure A.P. and 4.05% with traces (2%) carbinol-contaminated A.P. was recovered.

One distills the unchanged ethylbenzol and obtains a residue. Finally the crude oxidation product which was obtained by the air oxidation of ethylbenzol (which consists of ethylbenzol, acetophenone, phenyl methyl carbinol and benzoic acid and a small tar-like residue) can be subjected directly to the dichromate oxidation. But one has to use in such cases larger amounts of dichromate than correspond to the carbinol, because the distillation residue uses up chromic acid.

b) Air Oxidation of the Ketone-Carbinol Mixture

The distilled ketone-carbinol mixture was aerated with air at 100-120°C in a series of experiments with admixture of various catalysts such as copper oxide, copper benzoate, cobalt naphtenate and cobalt benzoate. Part of the carbinol is oxidized thereby, but pure acetophenone cannot be prepared in this manner.

The best catalyst was copper benzoate. In a half technical charge 270 kgs. of distilled ketone-carbinol mixture with a solidifying point of 9° were oxidized with air in the presence of 100 grams of copper benzoate. In the course of 17 hours the solidifying point rose from 9 to 16.5°C. That

means the carbinol content fell by a further air oxidation from 23 to 7%. The last 7% could not be oxidized further through additional blowing in of air.

c) The After-Oxidation with Diluted Nitric Acid

Pure phenyl methyl carbinol was used for these oxidation experiments which was oxidized at a mild condition with 14% nitric acid. Thereby, one obtains only oxidation products which were only slightly nitrogen-containing with a solidifying point of about 11.3°. No oxidation product which solidifies higher could be obtained. Also, when this method was transferred to the ketone-carbinol mixture, no unobjectionable A.P. could be prepared.

d) Fractional Distillation

The ketone carbinol mixture (about 20% carbinol) could not be separated in the laboratory in vacuum with ordinary distillation installations. There was some accumulation of acetophenone in the pre-out, but no pure A.P. of a solidifying point of 19.5° could be prepared. Also in the operation distillation one observed that the solidifying point of the various fractions decreased in the course of the distillation. In a distillation of a mixture of a solidifying point of 9.9° (thus a content of about 21% carbinol) the solidifying point of the distillate decreased to from 15.3 to 4.5°, that is, the first fraction contains only about 10%, the last 32.5% carbinol.

After these observations we developed a distillation apparatus in the laboratory which made it possible to separate a ketone-carbinol mixture (with 20% carbinol). It has a glass column of 1,950 mm length and 40 mm. diameter which could distill 50% of a pure acetophenone with a speed of 100 grams per hour. (solidifying point 19.2 to 19.5°). The reflux ratio was not measured. Also pure phenyl methyl carbinol with a solidifying point of 21.5° could be obtained from the mixture of 95% carbinol and 5% ketone.

One found in the laboratory experiments that the porcelain Raschig rings are not suitable. Further one observes that the solidifying points lie too low although the sulfuric acid test was all right. We assume that the porous porcelain Raschig rings hold the water which goes over first, and only slowly give this up again, so that the solidifying point was depressed by the water that was carried along.

In order to test the distillation on a larger scale the following distillation apparatus was built. An iron nickel-plated kettle of 150 liters content served as still. The column consisted of 8 iron rings with a total height of 10 meters. Each ring was 1,250 mm. long and had a diameter of 100 mm. and a filling height of 1,100 mm. Iron Raschig rings of 12 x 12 mm. were used. The dephlegmator was a small pipe cooler.

One distilled at a vacuum of 10-15 mm. The pressure drop in the column amounted to 50 mm, and rose towards the end of the distillation to about 90 mm. The reflux ratio was 3:1, in which the natural reflux which is relatively large in small columns was not measured inclusively. The oil bath temperature was 155°, and 2-2.5 kg. were distilled over per hour.

The acetophenone had a solidifying point of 19.3-19.5°. Towards the end of the distillation the oil bath temperature was raised to 195°. The temperature in the still was 132°, towards the end of the distillation 150°. The boiling temperature is 79-37° at 10-15 mm.

Distillation results: charge 120.0 kg. acetophenone-carbinol mixture with a carbinol content of 20%.

- 1) 5.7 kg. = 4.8% ethylbenzol and traces of styrol.
- 2) 77.4 kg. = 64.5% pure acetophenone (solidifying point 19.3-19.5°).
- 3) 22.0 kg. = 18.3% acetophenone plus carbinol.
- 4) 6.5 kg. = 5.4% residu.
- 5) 8.4 kg. = 7% loss (mostly in the ring packing).

This is a total of 120.0 kg. which = 100%.

At the end the mixtures at #3 above consisted of 90% phenyl methyl carbinol and 10% acetophenone.

e) Fractional Crystallization

The fractional crystallization was carried out first in the laboratory, later on half-technical scale and finally in a few technical experiments at Griesheim. It yielded better results on technical scale than in the laboratory. Pure acetophenone can be prepared by freezing out. It is true the processing of the mother liquors into pure carbinol and the further oxidation of these liquids with air in order to convert part of the carbinol into ketone is still difficult.

f) Separation Through Complex Formation

In the course of experiments about the conversion of the carbinol which is contained in the oxidation mixture into the relatively low-boiling styrol by means of phosphoric acid, it was observed that acetophenone forms an addition compound with concentrated phosphoric acid which crystallizes easily and melt at 80°. It decomposes upon heating with water and yields pure acetophenone with a solidifying point of 19.5°. But this separation requires molar amounts of phosphoric acid, and the carbinol cannot be isolated easily as such or in form of pure styrol. It is usually converted to polystyrene. Therefore, this method was not studied further.

g) Dehydration of Carbinol

As we have mentioned before, we observed in experiments about catalytic dehydration of the carbinol portion, by means of air with copper catalysts, that carbinol goes into styrol easily by splitting off water. It can easily be separated from acetophenone by distillation. Thus dehydration was studied by us in detail.

The first experiments were carried out in a tube of 3.5 cm. diameter and about one meter of filling length. The catalyst space was about 0.8 to 1 liter. After various experiments we found the silica gel B(4-6 mm) was the best dehydration catalyst. Also for continuous use silica gel is suitable. Besides pumice, pumice impregnated with Al_2O_3 , and molded aluminum oxide were tested.

250 g. per hour could be put through the tube mentioned above. 300-310° and 150 mm. pressure were the most favorable conditions. The reaction went, to be sure, at 250-280°, but the performance of the pipe is lower at that temperature. At higher temperatures like 330° decomposition occurs, with more intensive brown color of the oil and light gas development occurs. The reaction product, which consists of acetophenone, styrol and water, is separated by addition of concentrated sodium chloride solution in water. One kg. of ketone-carbinol mixture (20% carbinol) yields about 27 g. of water in one throughput. The crude product is separated by distillation in a column. Thereby one obtains about 90% of the charged ketone and 90% of the styrol that is to be expected. In addition to that one gets a few intermediate cuts which can be charged again in the next distillation. The residue of 3-4% remains containing: about 1% acetophenone, about 1% dypnone, 0.5-1% of 2,4-diphenylfurane, and 1.35% triphenylbenzol, and about 1% of resinous materials.

The other catalysts which were tested were less suitable. Thus pumice is almost ineffective at temperatures up to 300° and also at 300-350° it is insufficient. Solidifying point of the acetophenone which is obtained is below 17°. Pumice with aluminum oxide acts somewhat better but the performance is still insufficient. Molded aluminum oxide (Ludwigshafen) is nearly ineffective up to temperatures of 200°, at 300-330° it is satisfactory. Above 330° by-products are formed such as hydrocarbon like benzol. The ketone yield decreases thereby.

After these investigations in laboratory, a few half-technical apparatuses were designed but only the last one is going to be discussed here. (Compare App. 4). Ketone-carbinol is charged continuously into a circulation evaporator. The ketone-carbinol passes a rotameter. Then it is evaporated in vacuum at 140-150 mm. The vapors pass over a superheater and then enter the catalyst apparatus. This consists of a tube bundle of 14 pipes which lead up and down in a chamber, and which are located in a stationary salt bath. The pipes are welded firmly to the bottom. On the top they are free in order to avoid strain in the apparatus. The heating is done either through heating coils, or better with gas. The temperature distribution is satisfactory. The largest difference in vertical direction in the salt bath amounted to about 3°, and in horizontal direction about 10°. The individual pipes are 2.5 meters long and have a diameter of 40 mm., this corresponds to a catalyst volume of 38 liters. 15-16 kg. of the catalyst (silica gel, B, 4-5 mm.) are always in-filled at one time. The apparatus stands in a room whose temperature is kept constant at 25° through heating. (acetophenone)

solidifying point 19.5°). The life span of the catalyst amounts to 10-19 days, with an average of 14 days. This depends on the carbinol content of the mixture put through. The less carbinol that is contained in a mixture, the longer the catalyst can be operated. The catalyst can be regenerated by burning off. The throughput in this apparatus amounted to about 30 kg. per hour which is 1 kg. per hour and 1 liter of catalyst space. In the experiments with the object to increase the capacity one observed much sticking together. It is to be assumed that liquid drops were carried along by the vapor which formed tar at high temperatures and thereby stopped up the pipes. Nevertheless, one could operate 40-50 hours with an hourly capacity of 55 kg. It is probable that with the installation of an impingement sheet between evaporator and the entrance into the catalyst pipe one could operate with greater performance.

The following numbers serve for the evaluation of the process.

1,885.6 kg. of a mixture were charged (the mixture had a solidifying point 15.2° , carbinol content 11%). The following were run in 67 hours thus with a hourly average of 28 kg.

1836.2 kg. acetophenone - styrol-water mixture = 97.4%
37.5 kg. of bottom (from the evaporator) = 2.0%
11.9 kg. loss = 0.6%

24.6 kg. of the mixture could be recovered from the distillation bottom, so that the total loss was 11.9 kg. plus 12.9 kg. which equals 24.8 kg. and corresponds to 1.3%. The acetophenone-styrol-water mixture can be separated easily by vacuum distillation. Thereby one obtains pure acetophenone with a solidifying point of 19.4° .

A number of processes have been worked out for the conversion of the crude ketone into pure acetophenone. But only the dichromate after-oxidation, fractional distillation and the dehydration is of technical interest. When cobalt compounds are used as catalysts for the air oxidation of ethylbenzol, the carbinol content of the crude ketone amounts to only 1-2%. Therefore, only the dichromate oxidation and the fractional distillation are the only ones to be considered for pure ketone manufacturing. In the dehydration method all too large amounts of acetophenone have to be used along with it. Because of the small carbinol content only relatively few chemicals are needed for the dichromate oxidation. The chroma liquor which is formed can be reconverted through precipitation with lime and oxidation of the precipitates into technical dichromates. Therefore, we prefer this method to fractional distillation at Uerdingen. Two distillations have to be carried out in the chromate method but in both cases they are only driving over. Neither in the ketone-carbinol distillation nor in pure distillation of the acetophenone does one need to fractionate carefully.

-12-

Acetophenone is a cheap intermediate product on basis of the described investigation. It induces experiments to find new fields of use for it. As first fruit of this knowledge we shall point out the acetophenone resin that was developed by Hills.

/s/ Pinkernelle and Kroning

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Hasche Reel 1, Frames 500-506
I.G. Farbenindustrie, Urdingen Plant, April 30, 1941
Scientific Zetko Exchange, Report by Dr. R. Mittag
About Catalytic Oxidation with Atmospheric Oxygen in Liquid Phase

II. Oxidation of Toluol and Chlorotoluens

The previous report showed that the new investigation of the catalytic oxidation of ethyl benzol brought good progress. These induced us to take up the investigation about catalytic oxidation in liquid phase on a broad basis. We shall report about the scientific and technical results in the following reports.

The auto-oxidation capacity of various organic substances, which has been known for a long time, directed us in these investigations. Substances that contain active centers in the molecule (phenyl, double bonds, ether oxygen, carbonyl) are particularly easily auto-oxidized. The oxidation of such materials is described in numerous publications. The oxidation of these materials and others compounds of almost all organic substance classes with catalysts or activators has shown that only increases in conversion and shortening of reaction time obtained in such a manner makes it usable for technical purposes. The oxidation method is very rich in the preparative field, which requires much care in this catalytic reaction. But it promises success. A number of factors are available for regulating the oxidation with molecular oxygen; catalyst, temperature, pressure, irradiation, reaction time, amount of reaction, solvent etc. These factors must be gotten to agree with the influences of the constitution of the particular material on the oxidation. Thus one can find favorable reaction conditions for almost all substances. Thus the often not uniform course of oxidation can be conducted into certain channels so that one obtains a preferentially desired oxidation product.

1. Catalytic Oxidation of Toluol in Liquid Phase

Benzoic acid is now prepared on a technical scale from toluol and from naphthalene. In the catalytic oxidation of naphthalene in the gas phase benzoic acid is formed as by-product. But it is actually prepared from the stable oxidation product of naphthalene, phthalic acid anhydride, according to a method that was developed simultaneously in Germany and in the U.S.A. In this process one mixes the crude phthalic acid anhydride vapors from the naphthalene oxidation with steam. The phthalic acid which is formed intermediately is decarboxylated with suitable catalysts. The benzoic acid which is prepared thus is not yet pure. The entire process is a waste of organic substances, but it is made economical by the low price of naphthalene. The ideal method is the conversion of toluol into benzoic acid. The benzoic acid is prepared that way to a small extent by acid hydrolysis of waste benzotrichloride from the benzoyl-chloride production, but mostly through toluol oxidation according to (?) - Malétra.

This leads primarily to benzoic acid sodium (sodium benzoate?) and chromoxidehydrate which is processed into chromic oxide green. In normal times the selling of both of these products causes no difficulties at the rate in which they are formed. But prohibition against the manufacture of chromoxide pigments makes it necessary to reoxidize chromoxide hydrate into chromate. Thereby the economy of the process is effected. In the course of the investigation about the catalytic oxidations one found that one can easily prepare benzoic acid by oxidation of toluene in liquid phase, also on a technical scale. This process deserves consideration because of the reasons described.

In principle the oxidation of toluol with molecular oxygen has been known for a long time. The auto-oxidation capacity of alkyl benzols in the light and the acid formation was observed first by Weger (2). Ciamician and Silber (3) determined that after a reaction time of one year in light and in presence of H_2O and air one can obtain up to 12% benzoic acid. Soon it was recognized that this process passes through a peroxide stage. It can be accelerated by adding organic catalysts like phenanthrenequinone or anthraquinone or also lime water, carbon or possibly metallic catalysts to the toluol (4,5,6,7).

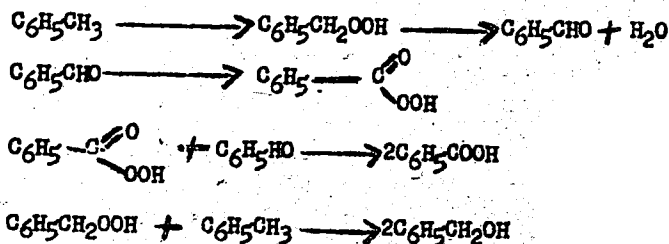
Processes for the oxidation of toluol in the liquid phase, in presence of metal catalysts in the form as set down in patents (8,9,10,11) was not used technically for various reasons. Walter (12) who first suggested gas phase oxidation of naphthalene with metal catalysts describes also first the oxidation of toluene into benzoic acid under these conditions. There appeared an abundance of patents (principally 13, 14 and 15) in America and Germany from which one can see that a stannous vanadium catalyst is best for this process which can easily be carried out. But the low naphthalene price and the quality of the benzoic acid formed have contributed to the fact that benzoic acid is not produced by this method today.

Our experiments have shown that benzoic acid can be prepared with good yields and in satisfactory quality by a simple reaction through oxidation of toluol in liquid phase. Numerous trials to oxidize toluol in presence of a cobalt catalyst at normal pressure and about $100^\circ C$ were unsuccessful, also the admixture of substances (nitrobenzol, ethylbenzol, nitrotoluol, anthraquinone) which induce or speed up oxidation under certain conditions changed nothing. Finally it was shown that a small sulfur content in the toluol caused the trouble and that the reaction can be carried out (although only slowly) under the mentioned conditions. By this method, the reaction velocity and the conversion are too small for a technical process. The relations are much more favorable with increased pressure and temperature, and we have tested the process in a small scale in a great number of experiments. Dr. Krey has carried out an experimental series with technical toluol in larger scale, and it was shown that these experiments proceeded still better and without difficulties (see table).

The reaction is carried out similarly to the oxidation of ethyl benzol, in such a way that a lively air stream is blown through the toluol placed with the catalyst in a tunnel tube at temperatures over 100°C and at a pressure of a few atmospheres. The start of the exothermic reaction shows itself soon in the air analysis and by water evolution. The water is condensed and separated, the toluene leaving with it is conducted further to the oxidation. A series of experiments is compiled in the table below.

Notwithstanding this reaction is so easily executed, still it proceeds relatively slower than the oxidation of ethylbenzene, or the xylols to be mentioned later. This shows itself in the longer oxygen absorption time, and in that the less effective catalysts, such as iron- or copper salts, are entirely without effect, while on the other hand the more effective catalysts, manganese and cobalt salts, possess the same effectiveness, and first of all make possible the carrying out of the process.

The following scheme is probable for the course of the reaction:



These formulas demonstrate first the auto-oxidation of toluol by way of peroxide formation, then they are supported by our knowledge in the cyclohexane oxidation and finally they allow recognition of the reaction products resulting. The principal reaction product is benzoic acid into which 50-60% can be converted without difficulty. After the cooling of the reaction products, the acid is precipitated in thick scales. The acid can be partially recovered by pressing out, and completely by alkaline extraction, also by distillation of the crude effluent a colorless quality is obtained, smelling somewhat of dibenzyl ether, however. The toluol again recovered is re-circulated to the oxidation without detriment. If the aqueous solution of sodium benzoate is treated with a little hypochlorite, or better with permanganate, a benzoic acid is obtained whose quality is satisfactory for all purposes. Benzaldehyde and benzyl alcohol can be obtained as by-products with this process, although these exist in amounts of a few percent. Likewise, some benzyl benzoate forms through a secondary reaction.

The process described represents the simplest way in which benzoic acid can be obtained from toluol and upwards. Its large scale use is dependent upon toluol price, and deserves attention, besides for benzoic acid production from naphthalene, also phthalic anhydride.

Toluene Charge Kg.	Catalyst Grams	Temp. °C	Atm. Abs.	Air/Hr.	Time Hrs.	H ₂ O	Product	Benzoic acid content on product
2-3	10 Co sol.	138	4	150 l	5?	?	2400 g	18%
2-3	10 " "	140	3	150 l	7	80	1750 g	29%
2-3	10 " "	158	5	100 l	10	122	2072 g	31%
2-3	10 " "	165	7	150 l	8	179	2040 g	43%
2-3	10 " "	168	7	150 l	7	132	2104 g	33%
2-3	Mn-Sol	150	4	150 l	6	70	2200 g	20% broken off
249	500 Co	135	4	9 m ³	24	20L	269 kg	53%
251	500 "	130	4	9 m ³	24	15.6	266 kg.	30% broken off
300	500 "	135	5.5	10 m ³	26	28	332 kg.	40% broken off

II. Catalytic Oxidation of Chlorotoluol

Toluol is much less inclined to auto-oxidation than, for example, ethylbenzol or the xylois. Such a property has not become known of chlorotoluols or, for example, of methoxytoluol or acetylcresol. Accordingly, these substances are oxidized with more difficulty than toluol. However the oxidation of chlorotoluol proceeds smoothly at temperatures above 140°C, thus below the boiling point of these materials. It is to be assumed from this that the reaction here also runs by way of the peroxide step, so we were surprised that the oxidation took place in the liquid phase still at so high temperatures.

Regarding the conversion of chlorotoluol to chlorbenzoic acid by catalytic oxidation, something is already known in the chemical literature. For instance, a process is described in which this substance is conducted over highly heated metallic oxide, and so becomes oxidized (16). As catalysts this process names thallium oxide, tin and other metallic vanadates. The reaction was investigated by Charlot (17) in all particulars. Likewise an oxidation method is described in I.G. patents. (18). The reaction is undertaken in autoclaves in the presence of water and metal oxides and hydroxides at temperatures over 200°C and at pressures of 50-60 atmospheres. Molecular oxygen also serves here as the oxidation means.

Through the presently conducted investigation it was shown that such an oxidation results from pure oxygen or through atmospheric oxygen if a suitable temperature is held, a suitable catalyst is employed, and the gas is conducted through the substance. Cobalt compounds have proved especially good as catalysts also here. The reaction is appropriately carried out at temperatures between 140°C and the boiling point (160°) of the substance. The water resulting from the oxidation is suitably distilled off, since otherwise precipitation of the catalyst may result. The working up of the reaction product proceeds like that described for benzoic acid. Most appropriately the aqueous solution of the sodium chlorbenzoate is treated with a little permanganate, thus obtaining a chlorbenzoic acid which is equal to all requirements.

The production of ortho chlorbenzoic acid by this process runs especially smoothly, since this remained molten at the reaction temperature; so that the conversion can be brought to about 80%. The para chlorbenzoic acid on the other hand crystallizes out from the mixture at its saturation point, during the reaction, since it has a freezing point of 243°C . It is best then to cool, separate the mother liquor, and conduct this again to the oxidation. By this process aldehyde and benzyl alcohol and ester result as by-products. Naturally meta chlortoluol and chlortoluol mixtures can be oxidized in the specified manner as well. The oxidation of para chlortoluol succeeds especially easily.

/s/ R. Mittag

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Report by Dr. R. Mittag

About Catalytic Oxidation in Liquid Phase with Atmospheric Oxygen

III. Oxidation of Polymethylbenzol

In the catalytic oxidation of the toluol or chlorotoluol an aromatic-bound methyl group is converted into a carboxyl group in a smooth reaction. The oxidation in liquid phase of polymethylbenzol is even easier to be carried out than with these substances. In these materials one can see clearly that the catalytic oxidation in the liquid phase can perform somewhat different than the gas phase. The oxidation of xylol vapors on metal catalysts yields a mixture of various substances. But now we can obtain in a nice manner monocarboxylic acids from polymethylbenzols. Also, partial oxidation products which could sofar only be prepared with tedious methods on a technical scale by way of synthesized nitrile or aldehyde can be easily obtained now. It is particularly surprising that the attack by the oxygen stops almost completely after the oxidation of one methyl group in the oxidation of the xylol because in general the introduction of a carboxyl group increases the reaction capacity of a methyl group.

1. Oxidation of the Xylol

From the isomeric xylol one can easily obtain the various toluic acids by air-oxidation in liquid phase. These substances were rather hard to obtain until now, and the cost price made use on the broadest scale impossible. The toluol acids were prepared till now by careful nitric acid oxidation of the xylol, through acid saponification of toluene nitrile or from the corresponding aldehydes. But Ciamician and Silber(1) observe that toluic acid can be formed from xylol through an auto oxidation process. From m- and p-xylol iso- and tere-phthalic acid are formed. They obtained about 30% of toluic acid in a six months irradiation in presence of much water. In this process anthraquinone may act as accelerator (2). The oxidation of the xylol in the presence of heavy metal catalyst and much water at high pressures (3) which leads to toluic aldehydes and acids cannot be carried out technically. Charlot (4) worked on the catalytic oxidation of xylol in the vapor phase and obtained a mixture of predominantly toluic and phthalic acids.

The pure isomers served as starting material for the oxidation experiment or a mixture of them or "Solvent naphtha". No difficulties were observed in the oxidation of pure ortho-, meta-, or para-xylols. The reaction started at once or within an hour. By the use of solvent naphtha the oxidation can be entirely eliminated, but the solvent naphtha can also be freed of disturbing

sulfur by the treatment with aluminum chloride and then it is easily susceptible to the oxidation. The admixture of dissolved cobalt salts are advised to be used as catalyst. Manganese salts are also quite effective. Copper, iron, or lead salts are hardly effective. Reaction is carried out in such a manner as it is described in the oxidation of the ethylbenzol or in the mono methylbenzol. A temperature of 110-130°C was found to be suitable, whereby normal pressure is sufficient. The oxidation is finished faster at higher temperatures, but there usually forms larger amounts of more highly oxidized products which are described below. From one kg. charges, the reaction was completed in general after 20-30 hours with an admixture of 1% of cobalt soligen and air-stream velocity of 60 liters per hour at a temperature of 115°.

The corresponding toluic acids are formed from xylol as predominant oxidation products. From ortho xylol ortho toluic acid is formed, the formation of phthalic acid was never observed. The conversion can be brought to about 60% but it is advisable to oxidize up to about 40%. From meta-xylol, meta-toluic acid is formed. In addition to it there is always formed some iso phthalic acid the amount of which depends upon the reaction time and temperature. In longer reaction and higher temperature its amount goes up to 10% of the oxidation product. Therefore it is practical also in this direction to break off the reaction at about 30-40%. Para xylol can be oxidized even more easily than ortho and meta xylol. Ortho or meta toluic acid remain in molten state during the reaction. The para toluic acid crystallizes out at its saturation concentration. It is filtered off after cooling of the solution and the mother liquor is brought back into the reaction.

The danger for terephthalic acid formation is particularly great here, therefore, one oxidizes only to a reaction of 30%. The acids that are formed from the technical xylol mixture melt at about 70-100°C, they contain about 100% phthalic acid. The by-products of the reaction are toluic aldehydes and methyl benzyl alcohols (each about 2-3%), as in the oxidation of the toluol and also as secondary reaction products methyl benzyl toluylate.

The processing of the charges can be done in various ways. The substance solidifies soon after the running out from the reaction pipe by crystallizing out of the toluic acids. These are taken out less practically with aqueous alkali. The neutral parts are taken off, and the oxidation is carried out again. After that the toluic acids are precipitated by distillation at normal pressure or by the use of a weak vacuum. Thus there obtained in a quality which is sufficient for all chemical uses. The distillation residue contains the phthalic acid. It is taken up in alkali and treated with chlorine and is then obtained in a satisfactory quality. The processing can also be done by bleaching the alkaline solution of the toluic acid with oxidation agents such as chlorine water or chlorine gas. The acids which are precipitated then are pure white. They can still be distilled, or in the form in which they are obtained they can be worked, for example, into acid chloride.

In this process the toluic acids, the closest relative to benzoic acid, has become easily available. At the same time a new use for xylol has been found. Not only the acid mixture which is obtained from the solvent

naphtha is of great interest because of its low cost price, but also particularly because its various isomers are now cheaply available in chosen amount to synthesis which cannot be carried out with benzoic acid.

2. Oxidation of Other Polymethylbenzols

Not only the xylols can be converted into carboxylic acid by this method, but also other polymethylbenzols can be easily oxidized that way. The mesitylene (1,3,5 trimethylbenzol) yields, for example, almost only mesitylene acid in the catalytic oxidation (2,3 dimethylbenzoic acid). When 500 gm. of mesitylene were used one obtained 250 g of the acid. The oxidation of the pseudocumol (1,2,4 trimethylbenzol) does not yield a uniform reaction product. From 300 g of pseudocumol 160 g of carboxylic acid mixtures were formed. If one fractionates this with steam, one obtains monocarboxylic acid very easily from the distillate. From these one isolated predominantly meta xylol acids (2,4 dimethylbenzoic acid) in addition to asymmetric ortho xylol acids (3,4 dimethylbenzoic acid). From the distillation residue or also from the crude acid mixture one can obtain a dicarboxylic acid mixture of a m.p. of 300° by redissolving in glacial acetic acid or naphtha. In this one could detect the 2 methyl tere phthalic and 4 methyl isophthalic acid.

3. Oxidation of the Chloro Xylol

4-chloro 1,3 xylol is the only reaction product by chlorination of meta xylol. From para xylol one obtains 2-chloro 1,4 xylol. Now it has been shown that these easily available substances can be oxidized readily by the method described. Thereby the chlorotoluic acids are obtained which were nearly unavailable until that time. The oxidation of chloroxylol runs easier and also at lower temperatures than that of the chloro toluol. From 4 chloro 1,3 xylol one obtains the 4 chloro 3 methylbenzoic acid, and from 2 chloro 1,4 xylol the 3 chloro 4 methylbenzoic acid.



Here it is particularly advisable to break off the reaction at an early stage because otherwise by-products are formed in larger amounts, such as chloro tere phthalic acid or chloro isophthalic acid. Otherwise no new problems occur as compared with the chloro toluol or the xylol oxidation.

Also these oxidation products have only been available by an expensive method. Therefore their further reactions deserve attention. The acids are partial oxidation products like the toluic acids and their further conversion into corresponding chlorophthalic acids through other oxidation agents is easy. Thus, one has the advantage, in the preparation of phthalic acid from xylols and chloroxylols, that the intermediate stages of the oxidation, toluic acids, are alkali-soluble compounds. They are easily attacked by other oxidation agents. Experiments are in progress to carry out the air oxidation to the stage of the phthalic acid.

/s/ Mittag

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