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INFORMATION DIVISION TRANSLATION T46-79

Hasche Reel 2
Frame 151

I.G. Farbenindustrie, Ludwigshafen, March 18, 1943
Scientific Zetkg Report 1943

Author: Dr. Flotz

Investigation of the Esterification Products of Triethanol-
amine with Higher Molecular Fatty Acids.

Stearic acid resp. oleic acid ester of triethanolamine are sold in trade as Soramin A base resp. Emulphor FM, oil soluble. One may expect that in the esterification at a molecular ratio 1:1 diesters and triesters also would be formed in addition to monoesters. Determination of unreacted triethanolamine by extraction with saturated sodium chloride solution made it possible to clarify the laws that control this esterification.

Thereby it was determined that only the monoester is formed first. If one maintains the esterifying temperature only for a short time an equilibrium exists which corresponds to an "equ 1 rights" to all hydroxyl groups that are contained in the triethanolamine and its esterification products. This is true for any desired molecular ratio for esterification. Thus the composition of an ester of 1 mol. triethanolamine and "x" mols of fatty acid is represented by the following formulae:

Mol.% free triethanolamine	$\frac{(3-x)^3}{3}$
Mol.% monoester	$\frac{x(3-x)^2}{3^2}$
Mol.% diester	$\frac{x^2(3-x)}{3^2}$
Mol.% triester	$\frac{x^3}{3}$

/s/ Flotz

Translated - Rochelle H. Bondy
Checked - Dec. 9, 1946 - GCM

INFORMATION DIVISION TRANSLATION T46-88

Maseno Riel 2, Franz 183

Ammonia Werke, Merseburg, April 1943

Scientific Zetke 1943. Merseburg #1. By Dr. Aisinger, Main Lab.

Chloro bromination of Aliphatic Hydrocarbons

The direct bromination of higher molecular aliphatic hydrocarbons is very difficult as it is known, since they are very slow to react with bromine. Also, very little hydrogen bromide formation occurs even when boiling, for instance Mepasin (from Kogasin II of the boiling range of 230-320 saturated by hydrogenation), with bromine under reflux. But bromination products are formed smoothly if one conducts an equi-molecular mixture of chlorine and bromine into mepasin and irradiates with ultra violet light. This occurs according to the general equation: $2RH + Cl_2 + Br_2 \text{ gives } 2RBr + 2HCl$. Alkyl bromide and hydrochloric acid are formed whereby one can introduce practically the entire bromine into the hydrocarbon molecule while the chlorine escapes with the hydrogen (compare I 70 438 IVd/120 = O.Z. 12,984). The reaction seems to occur by way of a compound of chlorine and bromine. The high molecular bromo-hydrocarbons produced in this way, which constitute a similar-isomeric mixture like the chlorination products, can, in contrast to the latter (since bromine confers more specific characteristics to the hydrocarbon than does chlorine), be extracted with the help of selective solvents from the mixture of bromination products and unreacted hydrocarbons. (compare O.Z. 14,030 = I 74 479/120). Acetonitrile is an especially suitable selective solvent for this extraction. It is true it can only extract relatively little bromination product each time. But its selectivity is very great. The chlorination product of higher molecular aliphatic hydrocarbons can be used for double conversion only in a limited extent, because thereby olefin formation occurs easily. The bromination product reacts much more smoothly, therefore their conversion will be investigated in the near future.

/s/ Aisinger

Translated Oct. 31, 1946 - Rochelle H. Bondy
Checked Dec. 9, 1945 - GCM

INFORMATION DIVISION TRANSLATION T46-89

Hasche Reel 2, Frame 101

I.G. Farbenindustrie, Ludwigshafen, April 14, 1942

Scientific Zetko Exchange 1942

Report by Dr. Schwcizer

Preparation of Alkyl Naphthols

The action of olefins (C_4-C_{11}) on beta naphthol, respectively tetralol, was investigated. Thereby, the corresponding alkyl, respectively dialkyl, naphthols were prepared.

First, a preparation process was worked out for the butyl naphthol from beta naphthol and isobutylene. In contrast to butyl phenol one operated without pressure and at lower temperature but with solvent.

The pure butyl naphthol--the position of the butyl group is not certain--is a compound which melts at $118^{\circ}C$ and crystallizes into colorless needles. Also, the dibutyl naphthol crystallizes into colorless needles and it has a melting point of 136° .

After that alkyl or dialkyl naphthols with longer alkyl remnants were prepared in similar manner by using the following:

Isosmylene, b.p. $28-50^{\circ}$ (about 90% of amylenes and 10% of hexylene)

Isohexylene

Isoheptylene

Isoamylenes-hexylene-heptylene, b.p. $28-95^{\circ}$ (10%:45%:45%)

Isohexylene-heptylene, b.p. $60-95^{\circ}$ (extra 1:1)

Isohexylene-heptylene octylene (45%:45%:10%)

Diisobutylene

Triisobutylene

Diheptylene

The olefins were derived from residue alcohols from Oppau methanol synthesis.

For the preparation of alkyl naphthols, beta naphthol is suspended in ethylene chloride, aluminum chloride is added (0.1 to 0.4 mols to 1 mol of naphthol), and the olefin is added either in gaseous form or in liquid (temp. $35-55^{\circ}$). The reaction solution is treated with water and the solvent is distilled off from the neutral washed solution. The alkyl naphthol which remains is used partly directly and partly after vacuum distillation.

The monoalkyl derivatives are (except butyltetralol) solid compounds with crude solidifying points between 45 and about 100° . The dialkyl products are very thickly fluid oils as the raw products. Dibutyl, diamyl, dihexyl-heptyl naphthols have been prepared.

The usability of numerous new products is still being tested. Butyl naphthol is of particular interest as stabilization agent for Buna, as far as it is used for colored technical articles. Further promising uses of alkyl naphthol are in the fields of textile agents, plasticizers, raw materials for varnish and dyes.

/s/ Schweizer

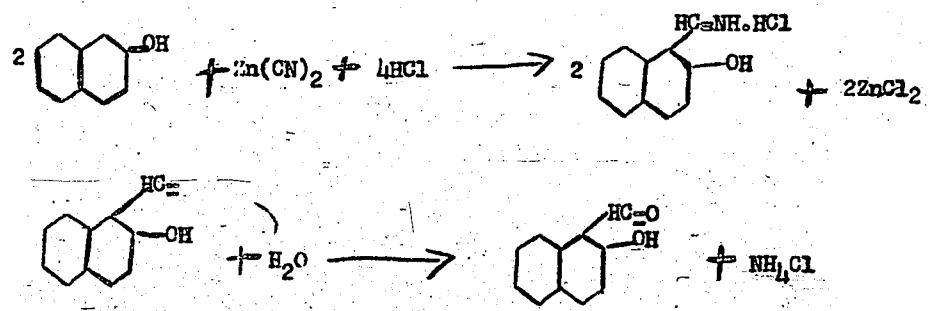
Translated Oct. 31, 1946 - Rochelle H. Bondy
Checked Dec. 9, 1946 - GCM

INFORMATION DIVISION TRANSLATION T46-90

Hasche Reel 2, Frame 404
I.G. Farbenindustrie, Ludwigshafen
Scientific Zetko Exchange 1942
Report of the Trifluorben Division (Dr. Kochendoerfer)
Technical Use of the Aldehyde Synthesis According to Gattermann

The Gattermann aldehyde process with zinc cyanide--hydrochloride was worked out for the preparation of 2(hydr)oxy-1-naphthaldehyde, the starting product for Lumogen I light yellow, and the resorcyaldehyde which is used for a few of the new CK leather dyes of our AZO division. It has been shown that it can be carried out with excellent yields without difficulty in a large scale and can probably be used also for intermediate products. Therefore, we shall briefly reproduce a few observations which are important for the synthesis.

The reaction course is as follows:



Benzol, toluol and particularly nitrobenzol have proved to be excellent dilution agents. The choice of suitable dilution agents is of decisive importance for the success of the reaction. The zinc cyanide is prepared in a degree of purity of 95-99% through precipitating the zinc chloride liquor with a cyanide solution at 80 to 95°. One obtains a white powder which can be stored for an unlimited time, which filters well, is not hygroscopic. It is used in finely pulverized form. One uses it usually in 30-100% excess over the theoretically necessary amount. All materials and the apparatus must be dry. As an example, the synthesis of the 2(hydr)oxy-1-naphthaldehyde shall be described briefly.

One fills benzol, 2-naphthol and zinc cyanide into a stirring kettle (enamel or iron) and adds gaseous hydrogen chloride in an excess over the calculated amount at 20-25°C. The reaction heat is very small. After 24 hours

one decomposes the aldiminichlorhydrate, which separated in crystalline form, with water. One dries off the benzol with steam after cooling one obtains the aldehyde in pure form. The yields of aldehyde distilled in vacuum is over 90% of the theoretical yield.

In similar manner we prepared the resorcyaldehyde, the 2,6 and the 2,3 di(hydr)oxy 1-naphaldehyde as well as the aldehyde from tertiary butyl phenol with equally excellent yields. We are, therefore, occupied to use the Gattermann process also for other phenols and phenol ethers. We also tried to investigate whether it cannot also be used for other products with active H atoms.

/s/ Kochendoerfer

Translated Oct. 31, 1946, Rochelle H. Bondy
Checked Dec. 9, 1946 - CGM

3

INFORMATION DIVISION TRANSLATION T46-91

Hasche Reel 2, Frame 445 - Höchst Plant, May 2, 1942

Scientific Zetko Exchange 1942

Author: Thomsen

Preparation of Benzyl Naphthalene

Till now naphthalene was reacted with benzyl chloride at 80-130° in presence of some zinc powder in order to produce benzyl naphthalene which is the starting material for tanning agents. The benzyl chloride must be quite pure because impurities in benzyl chloride lead to red colored tanning materials.

The difficulties in securing benzyl chloride motivated the experiments to produce benzyl naphthalene directly from toluol, chlorine and naphthalene, without previously isolating and purifying the benzyl chloride. These experiments led to the following processes.

Naphthalene, toluol, and zinc powder were mixed in a flask and heated to boiling. The toluol vapor is reacted with chlorine in a chlorinating space which is illuminated by Vitalux lamps. The benzyl chloride which formed and the excess toluol are condensed to a cooler above the chlorination space and they run back into the flask. The escaping hydrochloric acid goes to absorption. In the flask the benzyl chloride reacts with the naphthalene in presence of the zinc powder. The toluol is distilled into the chlorination space again in order to be reacted again with chlorine.

When the reaction is completed the benzyl naphthalene is ready for sulfurizing.

According to this process the benzyl naphthalene is considerably cheaper than that obtained by the old operation method from benzyl chloride and naphthalene.

One can also work with xylol in place of toluol. Thereby one obtains xylol naphthalenes in place of benzyl naphthalenes which can also be used for the production of tanning materials.

The process has been carried out successfully on a half-technical scale with toluol and xylol in several charges.

/s/ Thomsen

Translated Nov. 1, 1946 - Rochelle H. Bondy

Checked Dec. 9, 1946 - GCM

INFORMATION DIVISION TRANSLATION T46-92

Hasche Reel 2, Frames 473-474.

I.G. Farbenindustrie, Frankfurt (Main) Höchst, Central Lab. April 23, 1942
Scientific Zetko Exchange 1942

Author: Dr. Schornig

About Hydrogenation Products of the Alkyl Phenols

Dodecyl phenol (Ludwigshafen) is used as softener for Igamide. Therefore it was natural to test the P-oils which are available and which are used here in Höchst as textile auxiliaries also for their suitability as Igamide softeners. We tried to attain softeners with even more favorable properties, starting from these alkyl phenols.

It seemed natural to hydrogenate the P-oils. This yielded alkyl cyclohexanols and in the case of isooctyl phenol it yielded isooctylcyclohexanol, which could be oxidized to isooctyladipic acid. When esterified with isooctylcyclohexanol it yielded a softener with good properties.

The following products were used in the hydrogenation.

1. Isooctylphenol, 2. P-oil, Do, essentially dodecyl phenol, 3. P-oil MIV, mostly a mixture of diisohexyl and diisheptyl phenol, 4. P-oil Tri, mainly triisobutylphenol, 5. N-oil MIV, mainly a mixture of diisohexyl and diisheptyl 2 naphthol.

The technical products were distilled in vacuum in a thin layer evaporator, in order to attain an unobjectionable taking up of hydrogen, and in order to brighten them up. The P-oils do not have sharp boiling points in the fractionation, although they are volatile in a small temperature range in the thin layer evaporator at sufficiently high temperature and suitable charge velocity.

The hydrogenation of P-oils was carried out with nickel catalysts in a horizontal stirring bomb with good yields.

The hydrogenated alkyl phenols were tested as softeners for Igamide in mixtures just as they were obtained, and their properties were compared with the corresponding aromatic compounds. Surprisingly, it was found that the characteristically good compatibility of the phenols with Igamide disappeared through the hydrogenation. Therefore, they cannot be used for the purpose that they were planned for.

In order to use them as softeners for other artificial raw materials and varnish materials it would be practical to esterify them, as it is described in the hydrogenated isooctyl phenol at the beginning of this report.

Information about the distillation of the P-oils and the hydrogenated products are summarized in the two following tables.

TABLE I

<u>Product</u>	<u>Temp. of Evaporation</u>	<u>Temp. of Vapor</u>	<u>Press. in Evaporator mm. Hg.</u>	<u>Yield of Dist.</u>	<u>No. Distillable</u>	<u>Water Olefin</u>	<u>Properties of Distillate</u>
Isooctyl phenol	150° (200)	110° (130-145)	0.5	72%	15%	--	Bright oil solidifies solid
P-oil Do	185	167-168°	1	89%	7.5	--	Bright yellow oil
P-oil MIV	200	180	3	89.5%	7	3%	" "
P-oil Tri	200	185	0.2	93	2.5	5%	" "
N-oil MIV	260	235-240	0.3	83	7.9	2%	Very viscous oil

TABLE II

<u>Product</u>	<u>Hydrogenation Temp.</u>	<u>H₂ Atmos. Absolute</u>	<u>Diluent Solvent</u>	<u>Press. Dist. mm.Hg.</u>	<u>Boiling Limits</u>	<u>Mainly boiling at</u>	<u>Properties of Product</u>
Isooctyl phenol	150	60-100	Methanol	0.5	90-150°	110-120°	Colorless oil weak odor
P-oil Do	150	100	Cyclohexane	0.3	80-177	134-155	Colorless thick oil
P-oil MIV	150	100	"	1.8-0.4	90-235	160°	Colorless oil
P-oil Tri	140-150	100-140	"	3-1.5	87-210	120-130	Colorless oil
N-oil MIV	160-170	60-100	"	0.9-1.2	75-240	over 200°	Very viscous light yellow oil.

/s/ Schornig

Translated Nov. 1, 1946 - Rochelle H. Bondy
 Checked Dec. 9, 1946 - GCM

Basche Reel #2, Frames 522-523.
Progress in the Manufacture of "Palatinol HS"

In the esterification of phthalic acid with "Intrasolvan HS," a significant excess of Leuna alcohol is necessary, since this mixture of alcohols of 6 or 7 carbon atoms contains important amounts of difficultly or unesterifiable constituents.

These alcohols, used in excess, must be removed as completely as possible to obtain a satisfactory quality of the end product. Steam distillation serves one hereto. Since now, these alcohols are miscible in all proportions with Palatinol, and the Palatinol itself has a very low vapor pressure, it is reasonable without further ado that the removal of the last residue of excess alcohol succeeds only by the use of very large amounts of steam.

Besides a considerable use of energy, the capacity of the apparatus is very unfavorably influenced by this time-consuming manipulation. For this reason, instead of steam distillation under atmospheric pressure, we have gone over to a vacuum steam distillation.

Apart from the vapor pressure of the components being raised by the diminishing of the atmospheric pressure, a further advantage results, that one can attain temperatures which lie considerably over 100°C by the use of 4 atmosphere cooking vapor (Trans: steam?) whereas in the customary steam distillation from a suspension of Palatinol in water one can scarcely reach the temperature of 100°C.

Experience now has taught that the excess of Intrasolvan is to be driven out practically without residue in considerably shortened reaction time with a third of the amount of steam used until now. One succeeds thereby in overcoming a disagreeable bottleneck of manufacture and making the most of the capacity of the other units of the plant, without residue.

We have established that the blow-off can be left off then, if the Palatinol is heated up to 110 - 115°C (Trans: second temperature not clear) by means of the steam nozzled-in in a weak stream.

The Palatinol, freed in this way from Intrasolvan, shows a fore-out of only 0.1% of constituents boiling below 225°C in the vacuum distillation at 20 mm., while before introduction of the steam-vacuum distillation the Palatinols still had on the average 0. to 0. % fore out.

As we have established, olefines form from the Leuna alcohols in important overall dimensions in side reactions with the esterification. These olefines partly form polymers, and as such are still more difficultly volatile than the Leuna alcohol. We consider these olefines as the reason for the severe yellow coloring of the raw Palatinol. A supplementary treatment of the Palatinol with a potassium permanganate solution is successful

in extensively destroying these olefines. (Trans: Partially illegible paragraph indicating roughly that due to the vacuum-steam distillation, the amount of extraordinarily valuable permanganate needed for decolorization can be reduced to 60% of that used earlier.)

For the removal of suspended materials and other impurities, in connection with the permanganate treatment, the Palatinol is dried in vacuum in the presence of decolorizing carbon and filtered therefrom. It is evident now that the decolorizing carbon, blown dry, still contains absorbed 30-35% of its weight of Palatinol. We have recovered these amounts several times in this way, that we washed out the decolorizing carbon with the Intracolvan recovered with the steam distillation, and further added these wash liquors to the vacuum-steam distillation. Thereby the overall yield of Palatinol HS was raised in noticeable quantity.

Since after the introduction of the vacuum steam distillation we could revert to about a third also with the TO carbon, we recovered from this source in the present production the after-all still right important amount of 12-15 tonnes per day.

The non-esterifiable alcohols are sent back to Leuna, and are there conducted to the naphtha synthesis. This use was possible only from that moment on when we succeeded in keeping out the trichlorethylene previously used in the esterification as azeotrope, and substituting with an olefine mixture of boiling point 95-115°C. This accumulates as a by-product of the Palatinol manufacture and is easily topped-off with the steam distillation. Since Leuna was not able to use the trichlorethylene-containing recovered alcohols on account of risk of catalyst poisoning, these must be eliminated earlier. After stopping this nuisance, however, up until now, about 800,000 kg. recovered no-longer esterifiable, olefins-containing Leuna alcohols have been made available for the naphtha production.

Information Division Translation T47-14
Requested by Information Division
Translated February 17, 1947 by C. C. Miller

"Fortschritte bei der Fabrikation von Palatinol HS"

Wissenschaftlich. Zetko Austausch 1942 I-G. Farbenindustrie A. G.
Offenbach Works. April 30, 1942
2 pages, no illustration.

Essoho Reel 1/2, Frames 524-526
Work Regarding "The Difficultly Esterifiable Portions of Intrasolvan HS"

In the production of Palatinol HS from phthalic anhydride and Intrasolvan HS, an excess of the latter is necessary for the reaching of satisfactory yields. This alcohol excess is necessary not only for showing the equilibrium to the ester-side, it turns out rather that a larger part of the excess does not have the power, under the esterification conditions employed, to react at all with phthalic anhydride. The charged excess of alcohol is recovered again almost completely after the end of esterification, the amount of this portion (internally designated as Intrasolvan HSW) amounts to 20 to 25% of the Intrasolvan HS charged into the esterification, the amount of it formed in Offenbach corresponds to about 50 tonnes per month.

The increasing scarcity of Intrasolvan, caused by heightened requirements in different sectors, calls for a most favorable possible and complete use also of this difficultly esterifiable portion. The HSW alcohol, except a small part which is successfully used as azeotrope in place of toluol in Palatinol recovery, is presently worked up in Leuna to naphtha by hydrogenation.

The constitution of Intrasolvan HSW is subject to severe fluctuations, on the average the content is:

Alcohol (Carbon-No. 6 $\frac{1}{2}$)	68%
Ether (Carbon-No. 15)	18%
Olefin (Carbon-No. 6 $\frac{1}{2}$)	14%

In these figures, the alcohol content is by determination of active hydrogen, according to Tschugaeff-Zerewitinoff, the olefin content by catalytic hydrogenation, and the ether content from the oxygen residue of the elementary analysis, with consideration of the alcohol content found.

The not-occurring esterification with ortho-dicarboxylic acids, the boiling limits, and (in contrast to secondary and tertiary alcohols) the difficultly-taking-place dehydration permit concluding in this case on predominately primary alcohols of severe degree of branching. The alcoholic portions of Intrasolvan HSW are esterifiable with certain monocarboxylic acids in distinction to ortho dicarboxylic acids - from which therefore a reciprocal steric hindrance of two ester fragments is concluded. The usability of that kind of ester as a softener will be tested, even if according to experience till now such a monocarboxylic acid ester in general possesses no favorable properties.

Attempts to isolate individual compounds from the Intrasolvan alcohols by precise fractionation lead to no result. The boiling curve of Intrasolvan HS showed practically no difference from the boiling curve of the other alcohols which are recovered again by saponification of Palatinol HS. Intrasolvan HSW naturally shows a variable boiling behavior

affected by the low boiling olefins and other portions.

The conversion of Intrasolvan HSW to the corresponding olefin HSW seems attractive inasmuch as in this way the three side-by-side substances - alcohol, ether, and olefin, are eliminated and thereby the waste product is converted in simple fashion to a compound suited to homogeneous reactions. Dehydration of Intrasolvan HSW proceeds smoothly with the help of the customary water splitters. Working with liquid phosphoric acid catalyst at temperatures of 175 to 200°C is most favorable, under which conditions the process may be set up continuously. It is determinative in this case that the residence time on the catalyst is not chosen too large, since otherwise polymerization of the evolved olefins occurs. The different character of the alcohols of Intrasolvan HSW provides that after one-time passage of the catalyst under the described conditions there still exist undehydrated portions. After distilling off the lighter-boiling olefins HSW, therefore, the residue still containing alcohol or ether undergoes the dehydration again. Practically all is converted to olefin after subsequent further distillation of the olefins and three passes in all over the catalyst. The life of phosphoric acid catalyst is extraordinarily large compared with solid, easily carbonized catalysts; yet after a long time should a subsidence of the action occur, then a regeneration of the catalyst is possible, by thinning with water and separating the oil.

From 900 parts of Intrasolvan HSW there result on holding the described conditions:

400 parts olefins HSW (up to b.p. 115°C)
190 parts olefins HSW (of b.p. 115°C ca. 150°)
190 parts polymerized olefin (b.p. > 180°C)
110 parts water

Olefin HSW is a light, mobile naphtha-like fluid of boiling range 70 to some 150°C. The density according to boiling range is 0.72 to 0.77. The viscosity at 20°C is 1 centistoke, at 50°C, 0.6 centistoke.

The amount of the polymerization product resulting from the dehydration can possibly be further lowered by changing the experimental conditions. By longer residence time on the phosphoric acid catalyst on the other hand, the yield of polymer rises so far that practically all olefin is polymerized. The same effect is attained with the aid of boron fluoride under the usual polymerization conditions. The polymerized olefins obtained are faintly yellow oily liquids. They consist in the main of dimeric and trimeric olefin HSW. The highest polymers, resulting only in small amounts, are waxlike brownish substances.

The boiling limits of the polymer mixture lie between 60 and 180°C at 0.6 mm Hg.

Molecular weight, carbon atom number and viscosity in relationship are evident in the following table:

M. W.	Carbon Atom No.	Viscosity in Centi-stokes			
		20°C	30°	40°	50°
204 (?)	Ca 13 (?)	3.0	2.4	2.3	1.7
340 (?)	Ca 20	51.4	28.2	18.1	12.4

Therefore, it is probably possible to use the higher polymers of olefin HSW as a lubricant.

Olefin HSW reacts in good yield with phenol in the presence of boron fluoride or aluminum chloride to form an alkyl phenol of average molecular weight 185 (=C 6 $\frac{1}{2}$ in the side chain) This alkylphenol furnishes the corresponding glycol ether after addition of 6 to 10 moles of ethylene oxide. This on its part displays good capillary-active properties, which are still improved by sulfonation with chlorosulfonic acid.

Substance	Concentration	Drop Number x greater than water	Wetting speed of wetting rags
alkylphenol C 6 $\frac{1}{2}$ 7 molethylene oxide	3 g./l.	2.3	45 sec.
do, sulfonated	3 g./l.	2.55	10 sec.

Olefin HSW therefore can well be established in the detergent field.

According to DRP 716,435 (I.G. Uerdingen) unsaturated dicarboxylic acid anhydrides are obtained by reaction of olefins with succinic anhydride under pressure and at high temperature. Also olefin HSW reacts under the same conditions with around 75% yield, referred to succinic anhydride charged. The anhydrides obtained give esters, after conversion with suitable alcohols. The esters show a good gelatinizing ability for Igelite. They are still under test at this time.

Further possibilities for using Intrasolvan HSW or the olefins are still being worked on.

/s/ Ahrens and Riebeth

Information Division Translation T47-15
Requested by Information Division
Translated February 17, 18, 1947 by C. C. Miller

"Arbeiten über die schwer veresterbaren Anteile des Intrasolvans HS."
Wissenschaftlicher Zetke -
Austausch 1942. I. G. Farbenindustrie A. G. Offenbach Am Main.
April 30, 1942, 3 pages, no illustration

INFORMATION DIVISION TRANSLATION T46-93

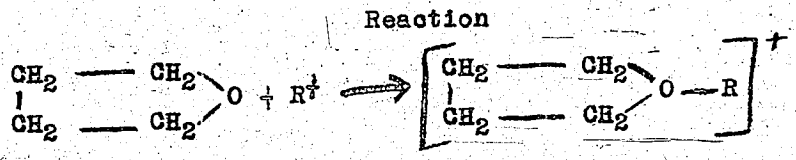
Hasche Reel 2, Frame 547 to 570
Leverkusen, Oct. 13, 1942
About Polymerization of Tetrahydrofurane
By. Dr. Delfs

Since Spring 1939 we worked on the polymerization of tetrahydrofurane in the Leverkusen Intermediate Products Laboratory. Prof. Meerwein, Marburg, observed that this material can also be polymerized. This material has been made easily available through investigations by Dr. Reppe. It has been used in many fields of utilization with great importance. Through personal contact we were informed of the new reaction early. We succeeded in getting the new process for the I.G., even though Prof. Meerwein worked with Schering. In the meanwhile we have developed the polymerization process with the cooperation of Prof. Meerwein. Its use has been studied (investigations of Dr. Morschel and Dr. Schulte).

Prof Meerwein observed in his investigation about tertiary oxonium salts that tetrahydrofurane polymerizes upon addition of such substances when heated. Today, we know a number of various catalysts which invoke the polymerization of tetrahydrofurane. One can summarize all that is common to all these investigations in the following polymerization theory which agrees with the total factual material that has been gathered so far. It shall precede the discussion of the experiment in order to make a clear arrangement of the materials possible.

Theory of the Tetrahydrofurane Polymerization

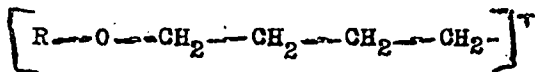
Tetrahydrofurane forms an oxonium ion under addition of a cation (for instance a hydrogen, alkyl or acyl ion) to the oxygen atom.



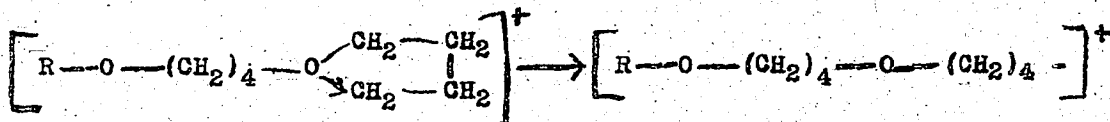
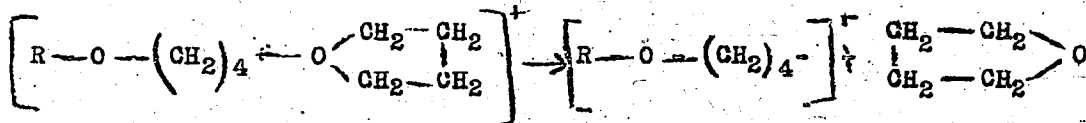
According to the manner of writing of the electron theory, this oxonium ion probably corresponds to one of the two following formulas:



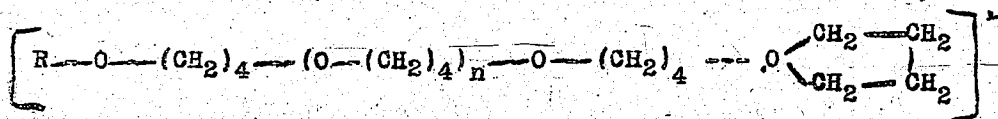
This manner of writing illustrates the reaction of the oxonium ion particularly well because it shows that one of the three attached groups of the oxygen is not "bound chemically" but that it has the character of an ion. The oxonium salts can act like the stable form of the unknown salts of alkyl ions. The following hypothetical alkyl ion would, for example, correspond to the oxonium ion of tetrahydrofuran.



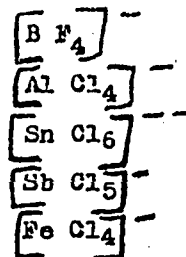
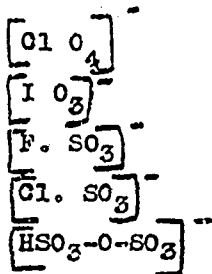
This assumed alkyl ion can be added to another tetrahydrofuran molecule, whereby a new oxonium ion is formed which showed the reactions of the starting ion, or of a new alkyl ion.



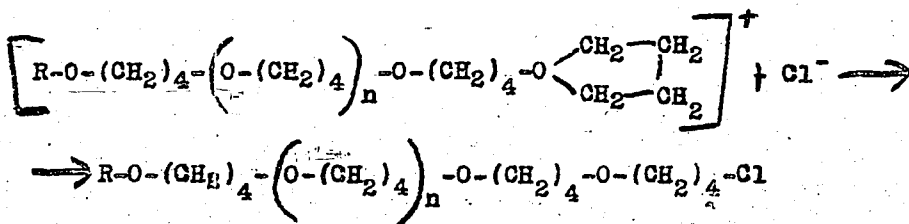
Either manner of reaction is possible. But the second reaction series predominates in the presence of a large excess of tetrahydrofuran. The new alkyl ion reacts with more tetrahydrofuran molecules in the described manner and it finally corresponds to a polyether oxonium ion of the formula.



The described polymerization reaction is tied to the oxonium ion. But the oxonium ion can only exist when the anion which belongs to it does not combine or unwillingly combines with an alkyl ion in order to form homopolar compounds. One can characterize such ions as electrophile. This condition is fulfilled by a series of complex acids, for instance:



But if anions are present in the reaction mixture which can easily combine with alkyl cations into non-dissociable compounds, such as halogen ions or the anions of other strong acids which are capable of forming esters, then these combine with alkyl cation corresponding to the oxonium ion.



Thus the polymerization chain is broken.

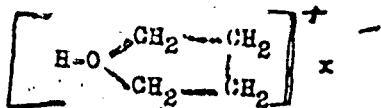
The theory for polymerization of the tetrahydrofuran that was presented makes a reaction course plausible which is characterized strikingly as ion-chain-polymerization, in contrast to other polymerization reactions.

Before discussing the practical carrying out of the tetrahydrofuran polymerization it shall be summarized again that this reaction occurs when oxonium salts of tetrahydrofuran can be formed, whose anions do not combine to homopolar compounds with alkyl cations under the experimental conditions.

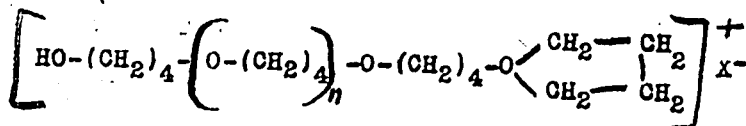
Carrying out of the Polymerization

The large number of possibilities to form oxonium salts of tetrahydrofuran for the initiation of polymerization can be summarized in a few groups:

1) Addition of a hydrogen ion to tetrahydrofuran - this case occurs if tetrahydrofuran is mixed with strong acids which do not form esters or which form esters only difficultly. Such acids are fluoro sulfonic acid, chloro-sulfonic acid, pyrosulfuric acid, hypochloric acid, iodic acid, ferric chloride-hydrochloric acid, aluminum chloride-hydrochloric acid. The two last acids are used to list simultaneous action of metal chloride and the equivalent amount of hydrochloric acid. It is assumed that oxonium salts of the following formula first form upon action of the acid named and tetrahydrofuran.



From this one obtains the following formula for the polymerizate according to the reaction mechanism of the ion chain polymerization.



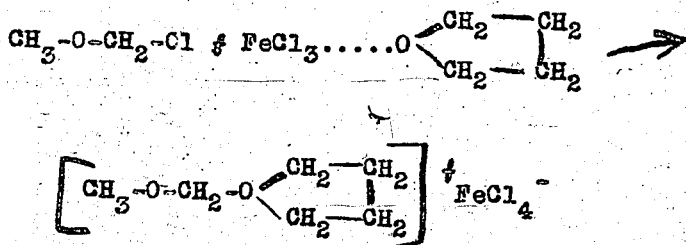
2) Addition of an Alkyl Cation to Tetrahydrofurane - The addition of an alkyl cation to tetrahydrofurane can occur in various ways;

Thru action of an organic halogen compound in presence of a suitable metal halide,

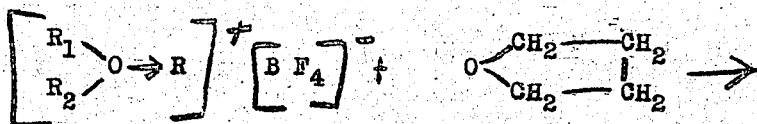
thru reaction of tetrahydrofurane with tertiary oxonium salts,

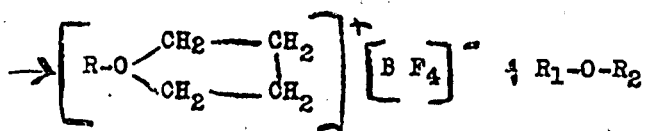
thru action metal halide on tetrahydrofurane.

There are only a few alkyl halogenides which are able to cause the polymerization of tetrahydrofurane with suitable metal halides. Alpha halogen ethers, like monochloridodimethyl ether and 2,3-dichlorotetrahydrofurane are particularly suited. Ferric or aluminum chloride have been most valuable in this case of halogenides. One cannot be wrong in assuming that the formation of a tertiary oxonium salt precedes the polymerization, for instance,

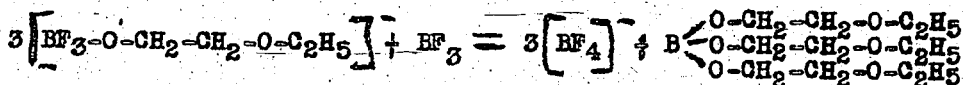
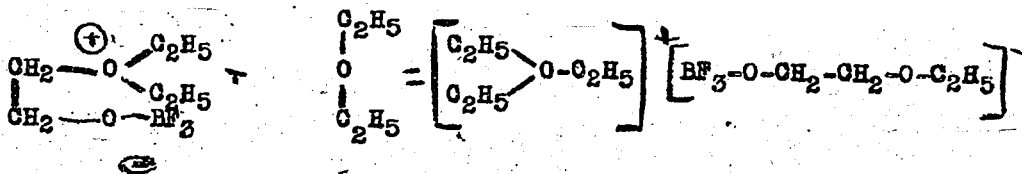
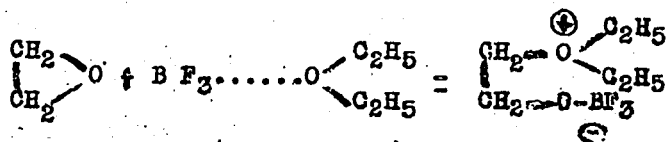


A smooth running polymerization is obtained if one allows tertiary oxonium salts to act on tetrahydrofurane. Thereby, oxonium salts of tetrahydrofurane are easily formed which are to be considered the beginning members of the polymerization, like

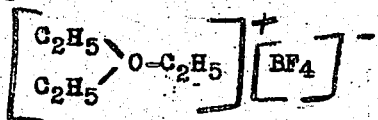




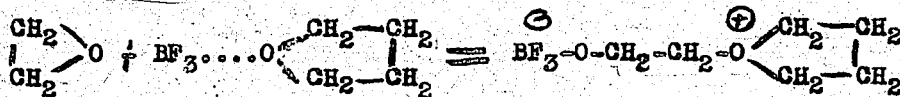
Tertiary oxonium salts are prepared according to Meerwein (Meerwein and associates J.Pr. 147, 257; 154, 83) by reacting suitable metal-and non-metal-halides like antimony penta chloride and boron fluoride on ether, in presence of ethylene oxide and its derivatives. The following reactions occur:



The end product is the oxonium salt:



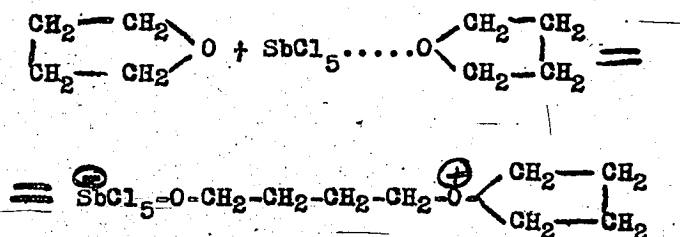
In this manner one can prepare tertiary oxonium salts of the following halogen acids: HBF_4 , HAlCl_4 , HSnCl_6 , HSbCl_6 , HFeCl_4 . The tetrahydrofurane is itself an ether. Therefore with the same reaction one can produce oxonium salt thru the reaction of ethylene oxide, respectively its derivatives, and suitable metal or non-metal halides on tetrahydrofurane and in this way polymerization of tetrahydrofurane can be caused.



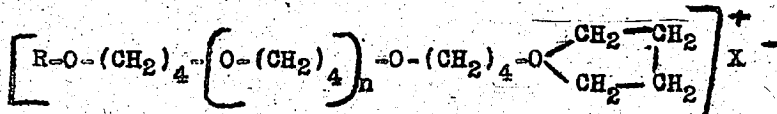
This polymerization method can be used in various places. Suitable components, for example, are:

BF ₃	ethylene oxide
AlCl ₃	propylene oxide
SnCl ₄	butylene oxide
SbCl ₅	epichlorhydrin
FeCl ₃	phenoxy propene oxide

One can further simplify the polymerization of tetrahydrofurane thru the action of metal halogenides on tetrahydrofurane. In this manner a practically usable polymerization speed can be attained, but only when antimony pentachloride is used. Hereto, the polymerization is probably started by a tertiary oxonium salt of the tetrahydrofurane. It is formed in analogous manner as by simultaneous use of ethyl oxide. A tetrahydrofurane molecule takes over the part of the ethyl oxide:

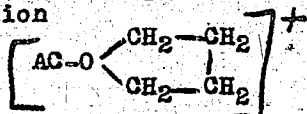


In all polymerization reactions that were described in which the oxonium salt of tetrahydrofurane is formed thru addition of the alkyl fragments to the oxygen atom of the tetrahydrofurane molecule, and which act as beginning member of the ion chain polymerization, the following formula stands for the polymerizate.



3) The addition of an Acyl Fragment to Tetrahydrofurane -

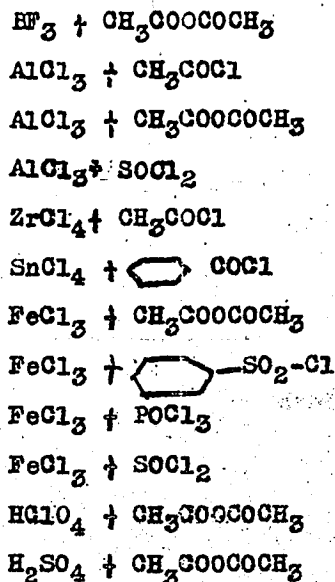
The third possibility for initiating polymerization of the tetrahydrofurane consists in adding an acyl fragment to tetrahydrofurane. Thereby, the oxonium ion



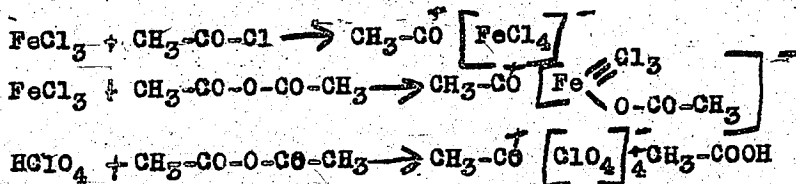
is formed which is to be considered the beginning member of the polymerization chain.

Practically this kind of polymerization is carried out in such a manner that the tetrahydrofurane is reacted simultaneously with electrophile

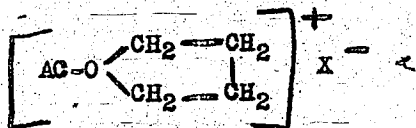
metal-or non-metal halide and acyl halide or anhydrides of organic or inorganic acids, or by using mixed anhydrides of such inorganic acids whose anion are polarizable with difficulty. A few possibilities are named here from the large number of suitable catalysts:



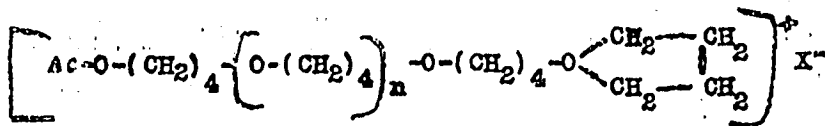
The catalysts are paired materials which result in compounds, in which anions of such acids are formed previously, like those which we know make polymerization possible. These possibly react in the following manner:



Apparently the general formula for the catalyst is $\text{Ac}^+ \cdot \text{X}^-$ and it is converted with the tetrahydrofuran into the beginning member of the ion-chain-polymerization.

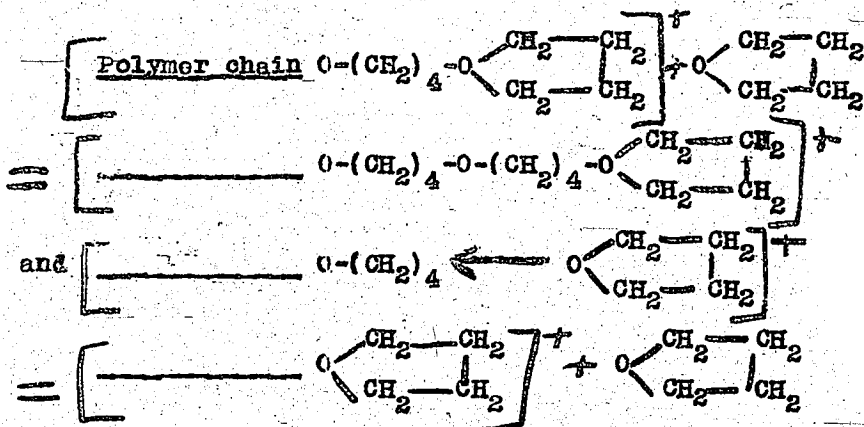


The polymerization product has the constitution



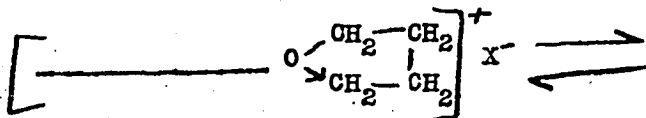
There exist easily hydrolyzable inorganic halogen compounds which act like acyl halides in the tetrahydrofurane polymerization. Altho they cannot be called acid halides if one wants to be exact, because the compounds that are formed in their hydrolysis do not contain the number of ionizable hydrogen atoms which corresponds to the number of halogen atoms of the halides. Such halides are SCl_2 , S_2Cl_2 , PCl_3 , PBr_3 , PCl_5 , AsCl_3 , SbCl_3 , TiCl_4 , ZrCl_4 , SiCl_4 , BCl_3 . Together with aluminum-ferric or stannic chloride they cause the polymerization of tetrahydrofurane in the same manner as the acyl halides that are mentioned above.

As one can see from what was said previously, there exist a large number of possibilities to polymerize tetrahydrofurane. The polymerization itself runs in the same manner in all cases, if one suppresses secondary reactions by cooling. The degree of polymerization of the product varies according to the reaction conditions. Externally one can recognize the progress of the polymerization from the increasing viscosity of the reaction substance. The final state is reached in hours or days depending on the kind and concentration of the catalyst. Apparently the polymerization goes to an equilibrium between the tetrahydrofurane and the polymerize which depends upon the concentration of the two products. If one worked without dilution agents then the polymerization yield is about 70%. If one disturbs the equilibrium by evaporation of the tetrahydrofurane, which can be found, for example, by using antimony pentachloride as catalyst, the polymerize is decomposed. Thus, it can be completely reconverted into tetrahydrofurane. Thus, the equilibrium seems to be characterized by the fact that the velocity of the two reactions are equal:



If the equilibrium is disturbed thru crystallizing out of the polymerize, then the polymerization reaction can proceed to a yield of 95%.

The polymerization velocity rises with increase of concentration of catalyst and monomeric tetrahydrofuran, and the temperature. Besides, it also depends upon the type of the catalyst, particularly upon the anion which acts in the reaction. This can be understood if one remembers the necessary inclination of the anion which is required in theory. They must remain in the ion state and must not combine with alkyl cations to form homopolar compounds (esters). This inclination must exist only to the extent that ions are present in the equilibrium which can promote the polymerization:



It depends upon the position of the equilibrium how large the actual cation concentration, and therefore the reaction velocity is.

Secondary reactions in the tetrahydrofuran polymerization

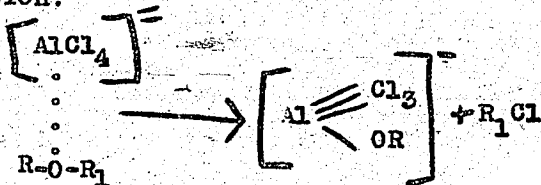
If the tetrahydrofuran polymerization is carried out at low temperatures, below 0°, one usually attains a smooth reaction course. At higher temperatures there are often remarkable disturbing influences. The investigation of the secondary reactions led to desirable methods to influence the properties of the reaction products.

The secondary reactions are caused by the great reactivity of the active complex anions which are effective in the polymerization.

The ClO₄-ion can oxidize and thus lose its effectiveness by being converted finally into the chlorine-ion which combines with a alkyl cation. Thus the ion chain is broken off, and the polymerization ends after all ClO₄ ions are reduced.

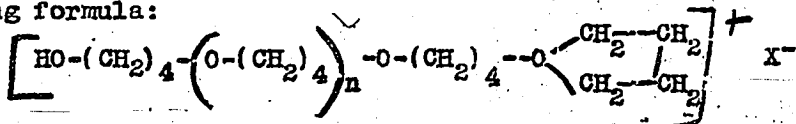
The anion of the halogen acids are inclined to decompose into halogen ion and halogenides in a varying extent, for instance, FeCl₄⁻ becomes FeCl₃ + Cl⁻. Since the halogen ions break up the chain, this reaction ends the polymerization. The stability of the halogen acid-ions decreases in the following order from left to right: SbCl₆⁻, BF₄⁻, FeCl₄⁻, AlCl₄⁻, SnCl₆⁻.

Probably the halogen acid anion can also be formed in the alcoholysis by acting on the ether group of the reaction mixture with a splitting action:

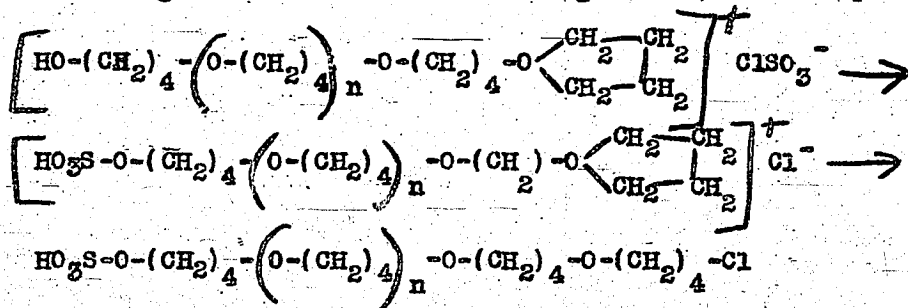


One can assume that such new ions are not very stable and have the properties in high degree to decompose with giving out of a halogen atom. If the alcoholysis occurs in such a manner that the polymerize chains are split, this decomposition can be noted in the decline of viscosity of the reaction mixture. This can be often observed if a polymerization is worked on after standing for several days.

If polymerization of the tetrahydrofurane has been initiated thru addition of hydrogen ion to tetrahydrofurane, then the polymerize has the following formula:



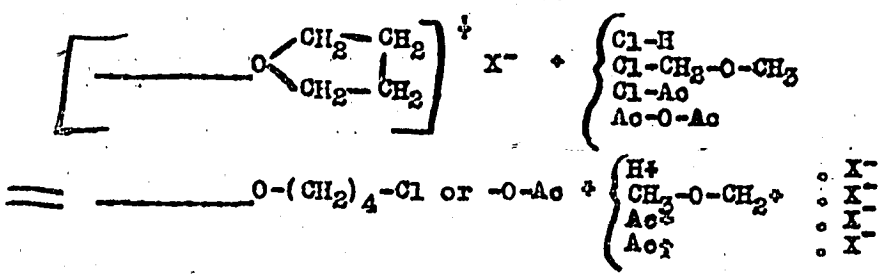
then the following possibilities will remain. The anion of the halogen acid can react with the OH group under alcoholysis and at least part of the reactivity may be lost. The behavior of chlorosulfonic acid is interesting in this respect. At room temperature the polymerization runs much faster than the reaction of the ClSO_3^- -ion with the OH-group. Only after standing for sometime the following reaction occurs possibly:



Thus, one obtains water-soluble sulfuric acid esters of the polymerize.

The secondary reactions in the tetrahydrofurane polymerization often cause a discontinuation of the polymerization chain in the following manner. Free halogen ions which originate from the decomposition reactions find the positive end groups of the reaction chain which are important for the progress of the polymerization thru formation of irreversible C-Cl bonding. Thus, one can succeed easily in breaking off the reaction chain in the tetrahydrofurane polymerization at will and to form new polymerization chains at the same time. For this purpose, one adds from the beginning compounds with easily movable halogen atoms like hydrogen halogen acids, alpha halogen ethers, and acyl halides, or acid anhydrides into the reaction mixture. These react with the poly ether oxonium salt by breaking the chain in such a manner that another catalyst results which causes the formation of a new polymerizations.

24



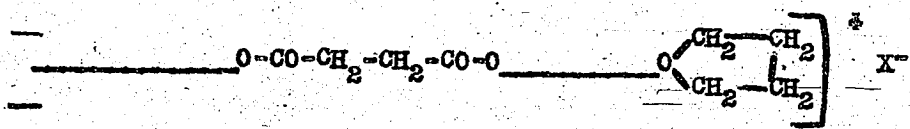
The compounds which are added to break the chain and simultaneously form new chains act in combination with electrophile metal- or non-metal halides which cause the polymerization of the tetrahydrofurane. This is done most practically by using the metal halides for the polymerization of the tetrahydrofurane from the beginning not in equivalent amounts (for example) acyl halide but in excess of that product. Particular valuable combinations are as follows:

BF_3 with excess acetyl fluoride,

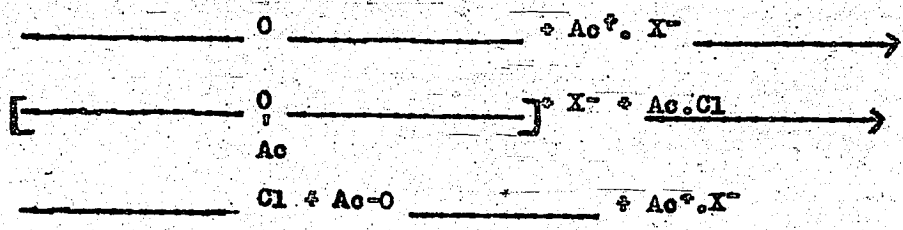
AlCl_3 or FeCl_3 with excesses of SOCl_2 , CH_3COCl or $\text{CH}_3\text{OCH}_2\text{Cl}$,

HClO_4 with excess acet anhydride or succinic acid anhydride.

Thus one obtains polymerizates which contain a number of smaller molecules in place of a longer polymerization chain. Thus this method is suitable for the preparation of low molecular polymerizates. If one uses bifunctional compounds like succinic acid anhydride as "breaching components", one obtains high molecular polymerizates which have succinic acids built in as esters.



It was observed that in many cases the molecular weight of the polymerization product falls severely when the polymerization has been finished. This is the case with anions of high polymerization velocity like $(\text{FeCl}_4)^-$. One can explain this decomposition of already formed polymerization chains into smaller cleavage pieces by the fact that the newly formed catalyst H^+X^- , Ac^+X^- , or $\text{CH}_2\text{-O-CH}_2^+\text{X}^-$ from the chain-breaking does not form new polymerization chains but attacks that chain at an oxygen atom, leading to splitting, for example:



The "breaching" or "decomposition components" are completely used up when the polymerization has worked for a sufficiently long period. One can

predict the average molecular weight through the amount of these components, and also the number of polymerization molecules. The amount of the second catalyst component, for instance, the metal halide, is only important for the polymerization velocity. An example may illustrate these conditions: a tetrahydrofuran polymerization was carried out at room temperature with addition of 2.5 mol.% FeCl_3 and 12 mol.% SOCl_2 , there resulted a polymerizate of the schematic formula $\text{Cl}-\text{Cl}$.

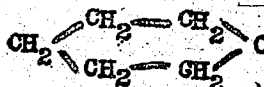
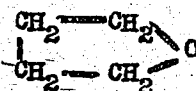
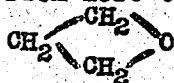
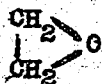
<u>Time of Reaction</u>	<u>Yield of Polymerizate in Grams from 100 g. of Reaction Mixture</u>	<u>% Cl</u>	<u>Average Mol. Wt. Calculated from the Cl Content</u>
1.5 Hrs.	34.0	2.7	2630
6.0 "	44.2	3.0	2640
22.0 "	52.0	9.9	714
3 Days	60.4	14.3	498
5 "	64.5	16.3	437

The average mol. wt. of 437 after 5 days that was found in this experiment is in good agreement with the mol. wt. of 478, which is required by the complete using up of the thionyl chloride. The fact that the mol. wt. is 9% lower than the theoretical one shows that the FeCl_4^- ion acts by partially splitting of the polymerizate under alcoholysis.

The decomposition of polymerizates can be done in the same manner either during polymerization or afterwards in the finished isolated products. It leads only in a small extent to functional derivatives of 1,4-butylene glycol even with large excess of decomposing agents. Obviously the ether group of the lower polymerizates (dimeric or trimeric) is considerably harder to attack than in higher molecular products.

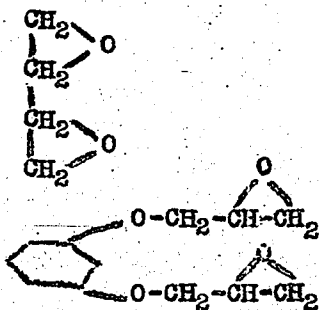
Mixture Polymerization of Tetrahydrofuran
With Other Cyclic Ethers

Until now one was concerned only with the polymerization of tetrahydrofurane, but one can assume that the polymerization of ethylene oxide and other 1,2-oxido-compounds which it is known can easily be carried out with the aid of acid catalyst could run in the same manner as the tetrahydrofurane polymerization. That is actually the case, but I shall not go into detail about this at this moment. However, it should be pointed out that also trimethylene oxide can be reacted in the same manner. Its constitution lies between that of ethylene oxide and tetrahydrofurane. On the other hand, the penta methylene oxide (tetrahydropyrene) is hardly polymerizable. The reaction capacity of the cyclic ethers decreases in the following order from left to right.

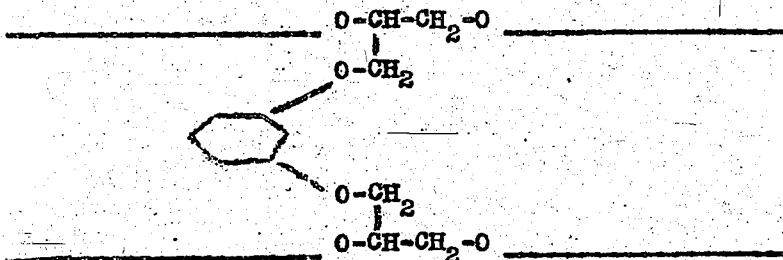


The substitution-products and homologs of all cyclic ethers react more slowly than the basic substances. Derivates of tetrahydrofuran could not be polymerized until now.

One can use up the reaction capacity of the 1,2- and 1,3-oxido-compounds for the preparation of mixture polymerizates with tetrahydrofuran. These mixture polymerizations are carried out with the aid of boron fluoride, antimony pentachloride, ferric chloride, or their combinations with decomposition components in any mixture ratio of the cyclic ether. It is like the polymerization of the tetrahydrofuran in all respects. One must see to it that the large reaction heat is carried off when one used ethylene oxide, which can polymerize very violently. Suitable 1,2-, or 1,3-oxido-compounds are: ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, epichlorhydrine, phenoxy propene oxide, butadiene dioxide, resorcin-bis-glycide ether, 1,3-propylene oxide, and others. The equilibrium of the mixture polymerization lies differently than in the separate polymerization of the tetrahydrofuran. The tetrahydrofuran is polymerized up to 90%, while the addition components are used up completely. In the mixture polymerization with bi-functional components butadiene dioxide and resorcin-bis-glycide ether, a new phenomenon occurs.



These compounds react in two different reaction chains.

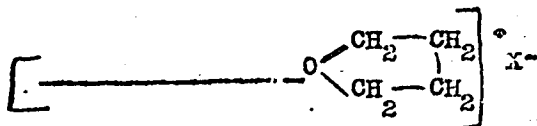


The polymerizates, which are usually built strictly in lines, formed nets.

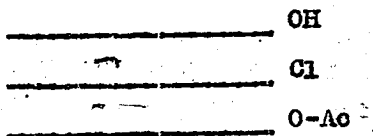
Isolation of the Polymerizates

Before we can discuss the properties of the tetrahydrofuran polymerizate, we must discuss the isolation of the products. The type of processing depends on the end groups which take the place of the oxonium grouping of the poly ether oxonium salts of the reaction mixture.

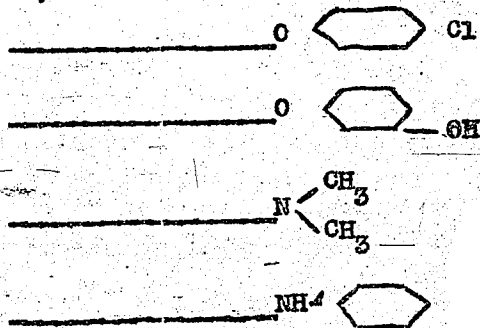
After completed polymerization the reaction mixtures contain the poly ether oxonium salts in addition to unchanged tetrahydrofuran.



They were formed in more or less large amounts of dissociated compounds, which performed undesired secondary reactions or desired chain-breaking or decomposition. The oxonium salts are very active compounds, as is already known from the investigations of Prof. Meerwein. They have the character of an energetic alkylation agent. In the aqueous processing of the polymerization products they can react with water or halogen-hydrogen acids (from the hydrolysis of halogen acid anions) or organic, respectively inorganic, acids (from the decomposition of acyl halides or anhydrides) according to the catalyst that was used. Thus the following end groups are formed:



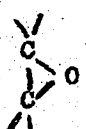
If the processing is carried out in alkaline partially in water-free medium, in the presence of easily alkylated compounds like phenols or amines, then these are built in as terminal groups in the polymerizate one obtains, for instance, the following end groups:



Constitution of Polymerizates

The polymerizates of tetrahydrofurane and the mixed polymerizates with 1,2-, respectively 1,3-, oxido compounds were built in lines, if no components were built in which form nets. Strictly speaking, they are not true polymers of the monomers m of the composition (m)_n. Moreover, they have the general formula in the separate polymerization of the tetrahydrofurane as follows: x-(CH₂)₄-O-(CH₂)₄-O_n-(CH₂)₄-y. The x represents the end group which is formed at the beginning of the polymerization, and y represents the end group which is formed at the breaking point of the polymerization, or during processing. The mixture polymerizates of tetrahydrofurane accordingly contain these ethers built in the chain with other cyclic ethers.

The following table contains the most important polymerization methods and the constitution of the polymerizates which are obtained in the aqueous processing, with regard to the end groups. The mixture polymerizates are not listed separately because they do not differ from the separate polymerization of the tetrahydrofurane in the nature of the end groups.

<u>Catalyst</u>	<u>End Groups</u>
(1) tertiary oxonium salts (R) ₃ O ⁺ X ⁻	$\begin{array}{c} \text{X} \\ \text{H}-\text{O} \end{array} \text{-----} \text{-----} \text{-----} \begin{array}{c} \text{Y} \\ \text{OH} \end{array}$
(2) BF ₃ + 1,2-oxido compounds	 $\text{HO}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\text{C}}-\text{O}$
(3) SbCl ₅	$\text{HO} \text{-----} \text{-----} \text{-----} \text{Cl}$
(4) AlCl ₃ + CH ₃ -O-CH ₂ -Cl FeCl ₃ + CH ₃ -O-CH ₂ -Cl	$\text{CH}_3-\text{O}-\text{CH}_2-\text{O} \text{-----} \text{-----} \text{-----} \text{Cl}$
With an excess of CH ₃ -O-CH ₂ -Cl	$\begin{array}{l} (\text{CH}_3-\text{O}-\text{CH}_2-\text{O} \text{-----} \text{-----} \text{-----} \text{Cl} \\ (\text{CH}_3-\text{O}-\text{CH}_2-\text{O} \text{-----} \text{-----} \text{O}-\text{CH}_2-\text{O}-\text{CH}_3 \\ (\text{Cl}-\text{O}-\text{CH}_2-\text{O} \text{-----} \text{-----} \text{-----} \text{Cl} \end{array}$
(5) AlCl ₃ + HCl FeCl ₃ + HCl SnCl ₄ + HCl	$\text{HO} \text{-----} \text{-----} \text{-----} \text{Cl}$
(6) AlCl ₃ + Cl-Ac FeCl ₃ + Cl-Ac SnCl ₄ + Cl-Ac	$\text{AcO} \text{-----} \text{-----} \text{-----} \text{Cl}$
With an excess of Cl-Ac	$\begin{array}{l} \text{AcO} \text{-----} \text{-----} \text{-----} \text{Cl} \\ \text{AcO} \text{-----} \text{-----} \text{-----} \text{OAc} \\ \text{Cl} \text{-----} \text{-----} \text{-----} \text{Cl} \end{array}$

- | | |
|--|--|
| (7) $\text{AlCl}_3 + \text{SOCl}_2$
$\text{FeCl}_3 + \text{SOCl}_2$ | Cl _____ Cl |
| (8) $\text{HClO}_4 + \text{Acetanhydride}$ | $\text{CH}_3\text{-CO-O}$ _____ O-CO-CH_3 |
| (9) $\text{SbCl}_5 + \text{ " }$
$\text{FeCl}_3 + \text{ " }$ | AcO _____ OAc |
| (10) ClSO_2H , processed alkaline
processed acid | $\text{HO-SO}_2\text{O}$ _____ Cl
HO _____ Cl |
| (11) FSO_2H Processed acid | HO _____ OH |

In the polymerization of metal halide + thionyl chloride, there should be formed polymerizates of the formula Cl-SO-O _____ Cl. But SO_2 is split off during the reaction and during the processing there results a sulfur-free polymerizate of the formula Cl _____ Cl. The mol. wts. of the polymerizates are in wide limits according to the polymerization methods used. The average mol. wt. is in indirect proportion to the catalyst concentration. One can obtain mol.wts. corresponding to a carbon value of over 100 with very small catalyst concentrations (down to 0.2 mol.%). But these high values can only be obtained when one uses the most stable anions like, for example, $(\text{BF}_4)^-$, $(\text{SbCl}_6)^-$ or $(\text{ClO}_4)^-$. These assure that the polymerization chain will not be broken prematurely because of some secondary reactions. If medium catalyst concentrations are used, one can obtain without difficulty mol. wts. corresponding to a carbon value of 30-to 70. One prepares low polymerization degrees suitably not through further increase of the catalyst concentration, but by the addition of breaking or decomposing components in the polymerization mixture.

Properties of Tetrahydrofurane Polymerizates and Mixture Polymerizates

Physical Properties

(a) Pure Tetrahydrofurane Polymerizate

The molecular construction of the tetrahydrofurane polymerizate in the form of unbranched chains allows a parallel straightening of the molecules. Thus the initially oily or viscous products mostly "crystallize" upon standing and become solid. But the crystallization speed is small and the softening point is below 60°C ., so that the use of the products as raw material for lacquer or artificial material is out of the question. The high molecular polymerizates (carbon value over 70) in the crystallized state show the known property of straight-built high molecular materials. Superpolyamide can be stretched up to a certain limit by straightening the molecules. The products are soluble in certain aromatic hydrocarbons, in aliphatic chlorinated hydrocarbons, in many ethers, esters, and ketones; it is difficultly soluble in aliphatic and cycloaliphatic hydrocarbons. The solubility decreased with increasing mol. wt.

Products with a high degree of polymerization corresponding to a carbon-value of 100, give very viscous solutions.

Products with lower mol. wts. corresponding to a carbon value below 16 remain liquid at room temperatures.

The consistency in solid state is vaseline-like in products up to a carbon value of 25, at a carbon value of 25 to 50 is wax-like, and at a carbon value from 50 to 100 is more and more viscous and horn-like.

(b) Mixture Polymerizates with 1,2-Oxido Compounds

The solidifying point is decreased considerably in the mixture polymerizates from tetrahydrofurane and ethylene oxide derivatives. The mixture polymerizates are usually oils with low solidifying points. They show solubility properties similar to pure tetrahydrofurane polymerizates, only the solubility in aliphatic and cycloaliphatic hydrocarbons with increasing oxygen content is still smaller than with the pure tetrahydrofurane polymerizates. In mixture polymerizates from tetrahydrofurane and ethylene oxide, one obtains finally water-soluble polymerizates with increasing ethylene oxide portion. The mixture polymerizates are net-like. These contain compounds with several ethylene oxide groups, like butadiene dioxide or resorcin-bis-glycide ether. They are more soluble in organic solvents and they have lost their plasticity.

Chemical Properties

Apart from the end groups which are capable of reacting in various ways, the chain molecule as polyether is stable against alkali and aqueous acids. They are unstable against such acid catalysts as are suitable for polymerization catalysts.

The tetrahydrofurane polymerizates are also unstable against oxidation agents like oxygen, nitrous gases; even oxygen of the air reacts without catalyst at raised temperatures (100-150°) whereby the oxygen content of the products rises. The products become more and more thinly liquid when the chains are split. They can be saponified with alkalis into water-soluble cleavage products. The points of attack for the oxidation are the carbon atoms next to the oxygen bridges. Thereby products of ester-like construction are formed. The oxidative decomposition through oxygen of the air is usually very undesirable. It can be prevented when small amounts of anti-antiooxidation agents (phenyl-β-naphthylamine, 4-cyclohexylaminodiphenylamine, styrophenol, and others).

You can use the end groups of the tetrahydrofurane polymerizates in order to introduce various kinds of groups by known methods. In this manner one attains a considerable change of the physical and chemical properties. In place of the end groups OH, OR, Cl, OAc, OSO₂H, which are obtained directly in the polymerization, the following groups were introduced.

From OH: O-R
 O-Ac
 O-SO₂-H
 Cl

From Cl: O-Ac
 O-R
 O-Ar
 $\begin{array}{l} R_1 \\ \diagdown \\ N \\ \diagup \\ R_2 \\ \hline C-N \\ \hline S-R \\ SO_3-H \end{array}$

From O-SO₃H:
 OH
 O-R
 SO₃-H

Utilization of Tetrahydrofurane Polymerizates

The polymerization of tetrahydrofurane and the mixture polymerizations with 1,2-oxido compounds can be carried out technically, easily with good yields in iron apparatus. You can also operate with the continuous process. The cost price of the polymerizate lies according to the manufacturing scale, 0.40 to 0.60 Reichsmark above the tetrahydrofurane price. The tetrahydrofurane cannot be used for the polymerization as it is delivered from the factory. It must be dry, and for some uses is must be specially purified. In general a distillation over potassium is sufficient. A particularly good purification, which serves well also in other cases, consists in the distillation with Grignard compounds.

Lacquer and Artificial Material Field

The tetrahydrofurane polymerizates cannot be used as artificial materials because their softening point is too low. But it is possible to use low molecular polymerizates for softeners, lacquers, and artificial materials. They are compatible with the following lacquer raw materials: nitrocellulose, AT Cellulose, benzylcellulose, pergut, bunalite, vinoflex. In the field of artificial materials the softening action is particularly valuable in contrast with Igelite PCU. The softened products have excellent cold resistance.

Tetrahydrofurane polymerizate with carbon values of 20 to 40 are suitable for plasticizing and for making sprayable Buna-S-mixtures. Until now, Buna-32 was used, and there is a noticeable lack of such products. The tetrahydrofurane polymerizates have the advantage over Buna-32 of a lower cost price. Starting from butylenglycol, one obtains, in addition, a considerably higher yield of polytetrahydrofurane sprayability agent than that of Buna-32.

Textile auxiliary Agent

Polymerizates which contain so much ethylene oxide that they are water-soluble on the one hand, and polymerizates with end groups that

make them water-soluble on the other, were tested as textile auxiliary agents. One determined a clear equalization action (partly similar to Peregol O) and also a softening action, particularly on Viskoses. The softening action approaches that of the fat-free Soromine FFA. But the effect is not wash-stable and seems, besides, to depend upon the moisture of the air.

The pure tetrahydrofurane polymerizates with carbon values up to 30 are suitable as leather-fattening agents. A product of a carbon value of 19 was announced as leather fat Le 254 at the CK. Compared with tallow, for which it is supposed to substitute, it has a greater absorption for water. This disadvantage can be eliminated by adding montan wax.

Patent Situation

The preparation process for tetrahydrofurane polymerizates was set down in the following patent applications:

Le 2457
2520
2521
2613
2918
2942
2979
2980

Four months after the application of our main application, Le 2457, there was issued a publication by Cloke and Pilgrim in Am. Soc. 61 2667, which describes the preparation of Chlorobutylacetate from tetrahydrofurane, acetyl chloride, and zinc chloride. Thereby, a small amount of 4-chlor 4'-acetoxy-dibutylether is formed as a by-product. This observation is in agreement with the experience of Ludwigshafen in the splitting of the tetrahydrofurane with hydrochloric acid in which also dichlorodibutylether is formed. Since we did not apply for patent applications abroad because of the war, our priority fell through. The American publication will force a limitation of our claims in the applications abroad, even though it is technically without importance.

Delfs

Information Division Translation T46-93
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Typed 2/2/47
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INFORMATION DIVISION TRANSLATION T46-80

Hasche Reel 2, Frames 589-595
I.G. Farbenindustrie, Uerdingen
Scientific Zetko Exchange 1941
Report by Dr. Binapfl
About: The Technical Preparation of Triisopropylbenzol

According to the literature triisopropylbenzol is formed by the following reactions:

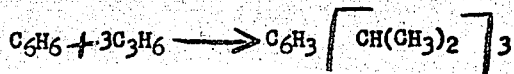
- (1) The action of isopropylchloride on benzol in presence of $AlCl_3$ (J. pr. Ch (2) vol. 72, p. 71; C.r. 140, 1940)
- (2) Reaction of propylene with benzol (a) in presence of catalysts of the Friedel Crafts type, particularly $AlCl_3$ (J. Am. Chem. Soc. 49/3142-49; 57/1547-58/ 919) Roczniki chem. 14/137-92; (b) in presence of concentrated sulfuric acid. J. Am. Chem. Soc. 58/910-922. J. Am. Chem. Soc. 60/2955-56.
- (3) Condensation of isopropyl alcohol with benzol in presence of concentrated sulfuric acid, boron fluoride, hydrogen fluoride or corresponding mixtures. (Monatsh. Chemie 53/54 721-52, Bull. soc. Chim. France (5) 1, 1494-98. J. Am. Chem. Soc. 62/1623-24.

Triisopropylbenzol is not formed as main product in any of the reactions mentioned. In addition to propylene polymerizates, one obtains only a mixture of various alkylation stages of benzol.

During my investigations about the synthesis of oil-compatible hard resins from the chloromethyl compounds of highly alkylated hydrocarbons, particularly from chloromethyl triisopropylbenzol (compare 33, Lacquer Commission Meeting, Sept. 29, 1941, Report Uerdingen.) it was necessary to develop a cheap method for producing triisopropylbenzol on a technical scale.

Based on the years of experience at Uerdingen in the field of alkylation of aromatic hydrocarbons, particularly naphthalene, we studied the action of technical propylene (Schkopau) on benzol in presence of aluminum chloride.

Orienting model experiments with pure propylene showed (after elimination of some difficulties in the beginning) the course of reaction as follows:



At optimum reaction conditions 60-64% of the benzol used, can be converted in one run into triisopropylbenzol. These conditions include pressure, temperature, stirring velocity, and dosage of propylene. This is contrary to information in the literature.

When commercial propylene(Schkopau) was used, the above yields could only be attained after a proper purification of the gases.

The propylation mixture is separated in the usual manner--by means of fractional distillation--into the various components. It is free of unchanged benzol and contains diisopropyl benzol and tetraisopropylbenzol as by-products. Also varying amounts of higher olefin polymerizates and small intermediate cuts are formed.

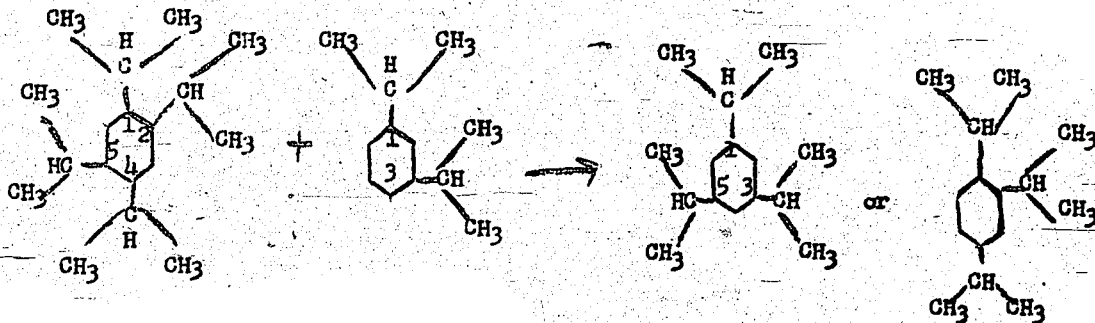
The tetraisopropylbenzol (C₁₈H₃₀) is a readily-crystallizing compound which accumulates in the distillation residue in the above process. Upon cooling it forms a crystal cake. (Yield 15-20% calculated on benzol used). Through filtering or centrifuging one can isolate it in rather pure form. The melting point of this product is 108-110° (literature 117-118°).

According to American investigations (comp. J.Am.Chem.Soc. 49/3142-49) its structure is a 1,2,4,5 derivative (oxidation to pyromellitic acid).

A series of orientation experiments to convert this interesting hydrocarbon into a technically useful derivative through various reactions (sulfation, chloration, nitration, oxidation by chromic acid or potassium permanganate) were negative so far. Nevertheless this course is still being continued.

Finally, one could determine that tetraisopropylbenzol in mixture with water-free AlCl₃ and the diisopropylbenzol that was mentioned above (contains 60-65% m-derivative) can be split into triisopropylbenzol through heating. The reaction runs quite smoothly (70-75%).

The course of reaction is made plausible by the following scheme.



The mixture consists of about 60-70% of 1,3,5 triisopropylbenzol.

The tetraisopropylbenzol is used up completely. Low alkylation stages of benzol (mono and diisopropylbenzol, compare patent application I 70,801 ivd/120) and small amounts of propylene polymerizates are formed as by-products. In the extraordinarily favored formation of tetraisopropylbenzol from di- and especially from trisopropyl benzol, the smooth course of the above reaction is theoretically surprising.

It seems to be a special case because the resplitting reactions of highly alkylated aromatic hydrocarbons which are known from theory and literature do not run as smoothly.

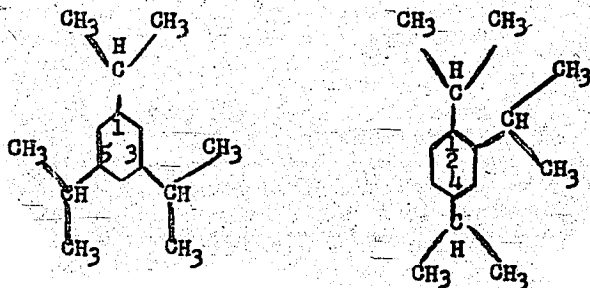
The technical preparation of trisopropylbenzol is arranged (so far discontinuous) into the following operation steps:

- (1) Action of propylene on benzol in presence of aluminum chloride.
- (2) Utilization of the by-products that are formed in (1).
 - (a) Splitting of tetraisopropylbenzol.
 - (b) Propylation of the low alkylation stages of benzol that were formed in (1) and (2a) in direction to trisopropyl benzol.

This described method of operation can be carried out without difficulties if suitable operation conditions are maintained as regards apparatus. Trisopropylbenzol can be prepared at present at a cost price of RM 0.60/kg.

The product will be even cheaper when the planned enlargement of the current experimental plant is carried out. Until now the total production is about 20 tonnes trisopropylbenzol. The chloromethyl compounds that were produced from it were processed partly (for internal purposes) to artificial resin 3086, and partly it was sent to Mainkur where it is used for the production of oil- and fat-free textile auxiliary agents.

The trisopropylbenzol obtained by this method is a water-clear slightly odorous liquid with a boiling point of b.p. $750 = 229-237^{\circ}$ which contains 1,3,5 trisopropylbenzol as a principal constituent. (oxidation to trimesic acid). There exists also an isomer probably with the structure of a 1,2,4, derivative.



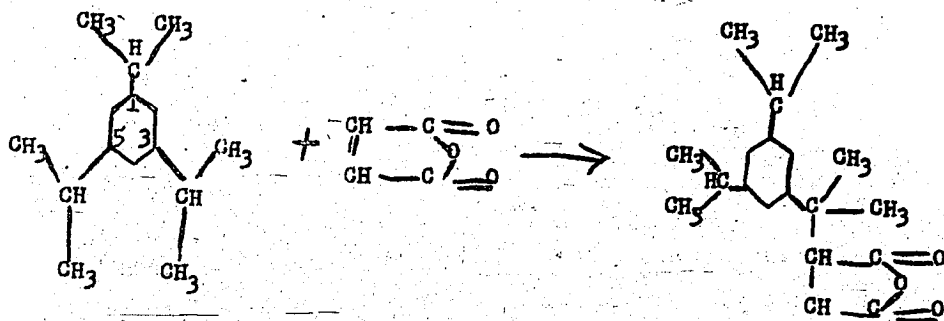
With regard to its preparation the hydrocarbon offers the opportunity for a series of reactions on the basis of its aromatic-aliphatic character and the three isopropyl groups.

Apart from the chloromethyl compounds that were mentioned before (compare Application I 58,033 IVc/12₀),



in addition to this the many years of investigation at Uerdingen about the utilization of alkylated aromatic hydrocarbons yielded the following results for triisopropylbenzol.

1. When reacted with maleic anhydride a diisopropyl- β -phenyl γ γ dimethyl pyrotartaric acid anhydride (yield 70-75%) is formed.



Thereby one deals with thickly liquid distillable compounds which are capable of numerous reactions at the anhydride groups. (DRP 607 380 and 623 338 and Zetko Report Uerdingen of Apr./16/34 VIII/117 and XI/99 of May/7/37.)

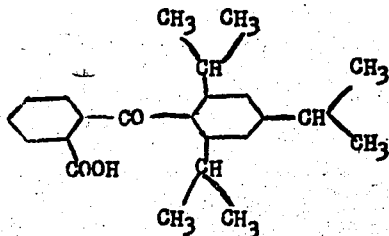
* They are distinguished by an extraordinarily good compatibility to naphtha. This property can also be transferred to its condensation products with components which are less soluble or principally insoluble in aliphatic hydrocarbons.

According to test by our Alkydal laboratory it is possible to convert, for example, R.D. alkydals that were prepared from pre-cut fatty acids, phthalic acid anhydride and higher alcohols into a naphtha-soluble form. These alkydals have the technical disadvantage of insufficient solubility in naphtha as compared with the linseed oil-containing alkydals. It is made soluble by substituting part of the phthalic anhydride (15-20%) by the anhydride named.

The general physical and chemical properties of the compounds are like those of alkylsuccinic acid anhydride from maleic acid anhydride and higher olefinic propylene polymerizates which I have been investigating for several years. (comp. Zetko Report Uerdingen of Mar./25/35 and DRP 716 435).

In spite of various technically valuable uses that have been found the commercial production has not been started. The calculated costs are too high, particularly because maleic acid is too expensive.

2. By condensation of triisopropylbenzol with phthalic acid anhydride in presence of $AlCl_3$, one obtains a clear, slightly yellow resin which probably contains a three times propylated benzoyl benzoic acid.



With regard to the lacquer industry (softening point, cookability with drying oils, water- and alkali-resistance of paints prepared from it) it is equal to colophony. But the cost is less favorable than natural resin.

3. The reaction with chloromethylated solvent naphtha yields, on the basis of new findings, resin-like condensation products. They are readily soluble in drying oils and aliphatic hydrocarbons. — In addition to a low cost price they have the advantage of valuable lacquer properties. (comp. application I 68,836 IVc/39 c).

The products named in (2) are surpassed by it in every respect.

Summary

1. Description of a process which makes it possible to produce triisopropylbenzol from propylene (Schkopau) and benzol at provisional cost price so far of RM. 0.60.
2. The triisopropylbenzol is a readily available, cheap building stone for organic intermediate products.
3. The operation field described is being developed systematically in the scope of the Uerdingen production with regard to apparatus and commercial production.

/s/ Binapfl

Translated Nov. 4, 1946 - Rochelle H. Bondy

Translated Dec. 11, 1946 - CGM