

1943

# The production of rubber from furfural

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**THE PRODUCTION OF RUBBER FROM FURFURAL**

by

**Llewellyn Wilson Burnette**

**A Thesis Submitted to the Graduate Faculty  
for the Degree of**

**DOCTOR OF PHILOSOPHY**

**Major subject: Plant Chemistry**

**Approved:**

Signature was redacted for privacy.

**In Charge of Major Work**

Signature was redacted for privacy.

**Head of Major Department**

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**Dean of Graduate School**

**Iowa State College**

**1943**

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TABLE OF CONTENTS

	Page
I. INTRODUCTION AND HISTORICAL . . . . .	1
A. The Hydrogenation of Furfural to Sylvan . . . . .	7
B. The Hydrogenation of Sylvan to Tetrahydro-sylvan . . . . .	15
C. Dehydration of Tetrahydro-sylvan . . . . .	18
II. EXPERIMENTAL PART . . . . .	23
A. Description of Apparatus . . . . .	23
B. Fractionation of Products and Calculation of Yields . . . . .	27
C. Action of Nickel and Alumina Catalysts on Furfural and Tetrahydrofurfuryl Alcohol . . . . .	29
D. Hydrogenation of Furfural to Sylvan . . . . .	33
E. Use of Large Apparatus for the Hydrogenation of Furfural . . . . .	45
F. Hydrogenation of Sylvan to Tetrahydro-sylvan . . . . .	50
G. Dehydration of Tetrahydro-sylvan . . . . .	57
III. SUMMARY OF RESULTS . . . . .	64
IV. LITERATURE CITED . . . . .	66
V. ACKNOWLEDGMENT . . . . .	68

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## I. INTRODUCTION AND HISTORICAL

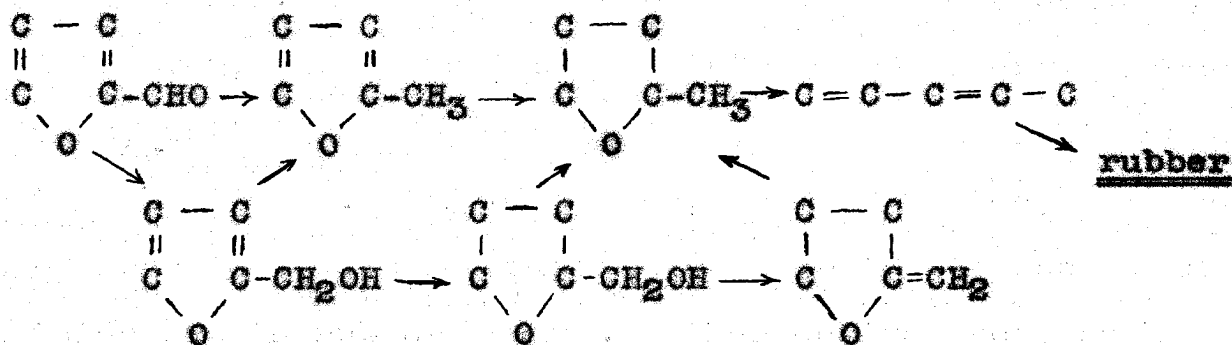
Since the advent of cheap furfural and the realization of its potentially huge sources around 1920, much investigation has been carried on in an attempt to find uses for it or its derivatives. In spite of its seeming potentialities, the studies have not advanced its commercial applications to a very great extent. Furfural itself is utilized in several limited ways: as a solvent, in butadiene and petroleum purification, in certain varnish resins and plastics, insecticides, fungicides, and as a paint remover.

The list of commercially available derivatives is surprisingly small. Furfuryl alcohol (used as a dye solvent, paint remover, and in resins) and tetrahydrofurfuryl alcohol (solvent, wetting agent, plasticizer) are available in commercial quantities. Hydrofufuramide, or furfufuramide, the product of reaction between furfural and ammonia, is used as a fungicide and in rubber curing. Other derivatives, such as furoic acid and furylacrylic acid, are available as laboratory chemicals but have no industrial significance.

Beginning with Padoa and Ponti in 1906 (1), the literature of furan chemistry is well-sprinkled with catalytic studies of hydrogenations and dehydrations, from which reactions any one or several of a large number of products may

be isolated. Padea and Ponti, by reducing furfural over nickel at 270°, isolated in the product sylvan, tetrahydro-sylvan, furfuryl alcohol, furan, pentanone-2 and pentanol-2. Depending on the catalyst and the conditions (liquid or vapor phase, temperature, pressure), other compounds such as 1,5-pentanediol, 1,2-pentanediol (2), tetrahydrofurfuryl alcohol (3), n-pentanol (4), and n-butanol (5) may be found in the product.

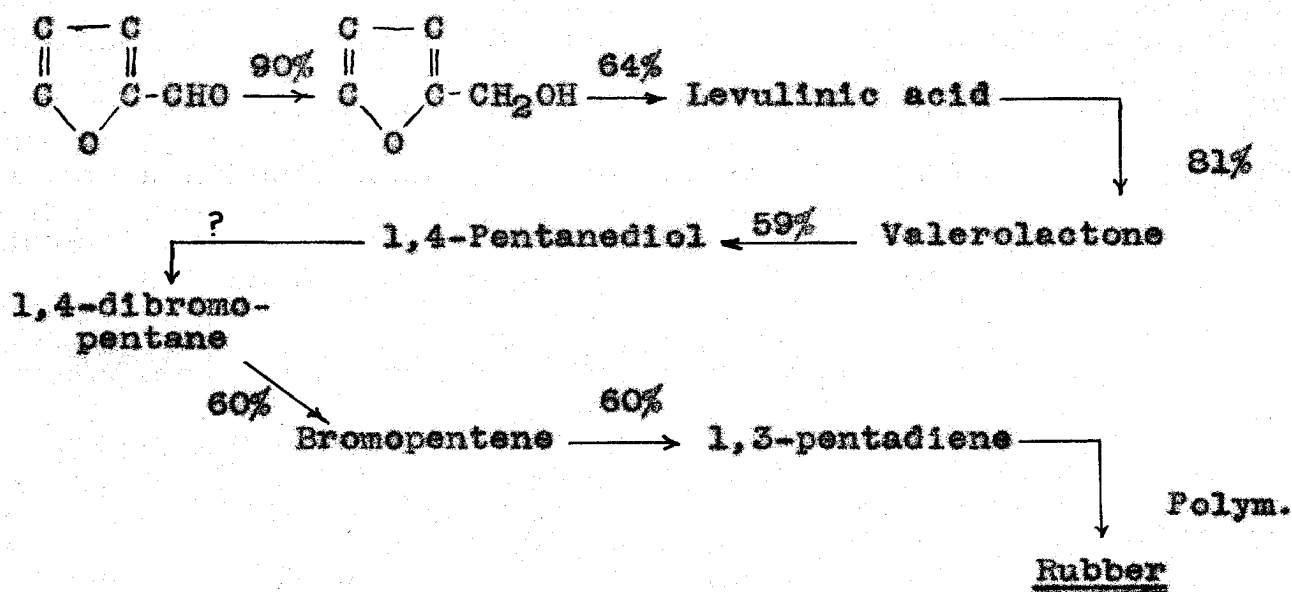
At the time when the rubber shortage was first being realized in the United States, it was noticed that a combination of several independent references exposed a possible rubber synthesis according to one of the following paths, and investigations of its possibilities are the theme of this study.



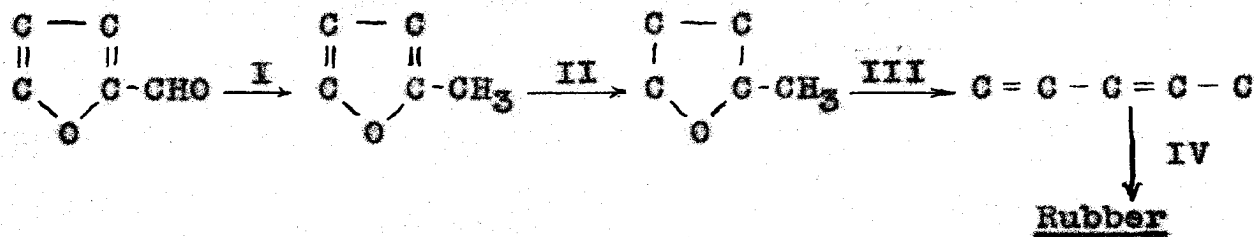
That this process had been conceived at least as long ago as 1936 was discovered subsequently when a patent was granted in the United States in February, 1942, (6) to a process which had been patented in France in 1936. Comparative references to this patent and the process as developed in this laboratory will be found in subsequent parts of this paper.



In Russia in 1939, A. M. Berkenheim and T. F. Dankova (7) published a study of the synthesis of piperylene from furfural with a view to use furfural as a source of synthetic rubber. Their approach consisted of several steps involving many expensive operations and chemicals and is obviously unsuited to commercial development for these reasons. Without the lengthy operational details, the process and yields may be diagrammed as follows:



The most feasible path developed here consists of the following four steps.



The production of the rubber hydrocarbon, 1,3-pentadiene,

from furfural is accomplished catalytically by two successive hydrogenations followed by a dehydration. The piperylene may then be polymerized to a rubber by any of the several existing commercial methods. The three catalytic reactions may be effected continuously in the vapor phase.

In the first step, the hydrogenation of furfural to sylvan, copper chromite has been shown to be very specific for the hydrogenation of the aldehyde group to a methyl group in the vapor phase, and yields of 95% sylvan in one passage over the catalyst have been observed.

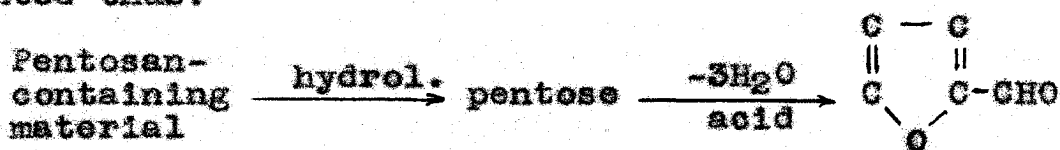
For the second step, Raney nickel only partially activated was one of the better catalysts discovered for hydrogenating the furan nucleus in the vapor phase. This it accomplishes in about 50% yield in one passage. The other products are chiefly pentanone-2 and pentanol-2.

The dehydration has been least thoroughly studied and is the least efficient of the three operations. It has been accomplished over several dehydration catalysts in yields up to 30%. Along with the 1,3-pentadiene, a comparable quantity of a 1,4-pentadiene fraction is produced, and it is thought that this may be converted to the 1,3-pentadiene by passing it over alumina at 300° to 400°. With further development, considerably higher yields are not hard to visualize.

Let us utilize these figures, along with the data on furfural supply and cost, to speculate on the commercial possibilities of agricultural waste products as a source of

synthetic rubber. The first point to be stressed is the fact that this source, as contrasted with the sources now utilized, is a waste product, and, as an agricultural by-product, is annually renewed. The alcohol and petroleum sources now being used are not waste products and are using up materials which are vital in many other processes. In the case of the rubber from petroleum program, its danger to the 100 octane gasoline production, so necessary at present, has already been vehemently suggested.

Any pentosan-containing material is a potential source of furfural. Its formation from these materials may be represented thus:

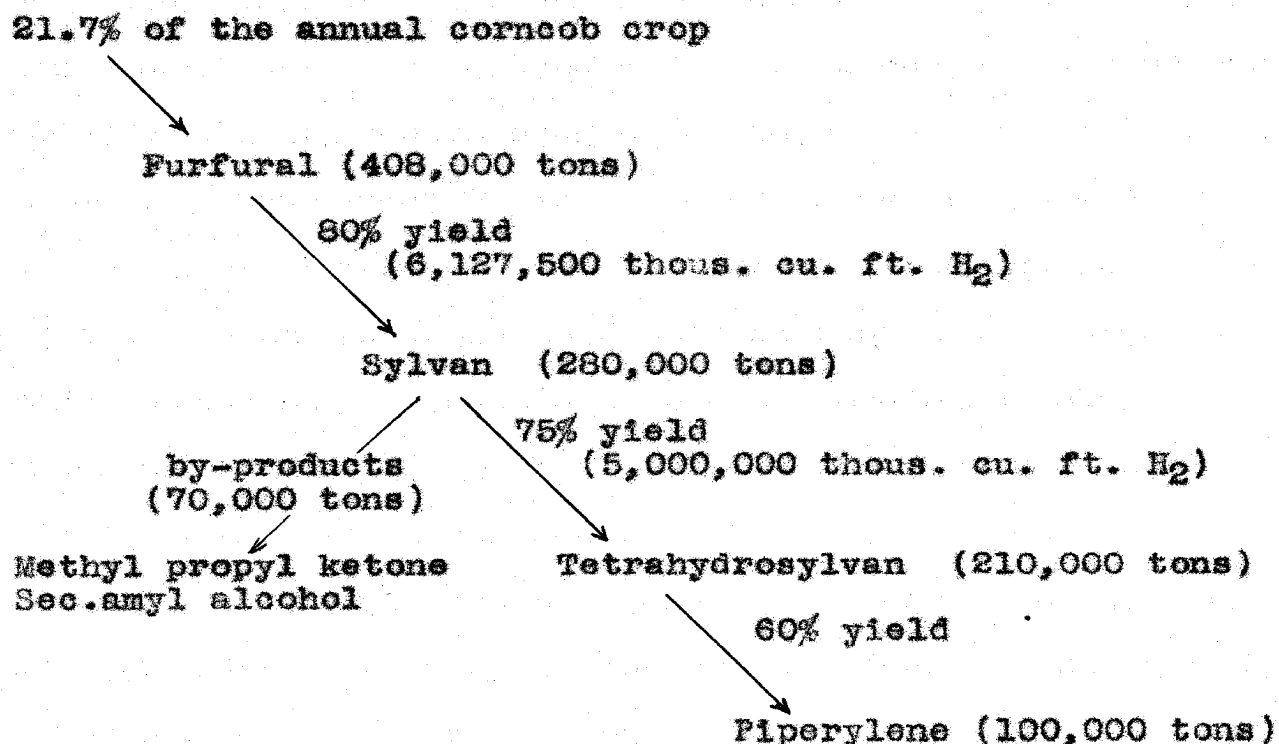


It has been estimated (8) that the total amount of furfural available in the United States is 50,000,000 tons. While securing all this would entail the collection of all the pentosan-containing material produced, the collection of only a small fraction of the total amount is practically possible and would furnish enough furfural for a full-scale rubber industry of hundreds of thousands of tons annually.

From \$30 a pound in 1920, the price of furfural has been lowered to \$0.09 a pound at the present time. In 1924, Mains and LaForge (9) outlined specifications for a plant which could produce furfural from corncobs at a cost of 6.15 cents

per pound. It is almost certain that in the nineteen years following that, even more economical processes have been devised. A Russian patent granted in 1940 to G. S. Surabekov and K. P. Likhushin (10) describes an industrial process consisting of catalytically hydrolyzing pentosan-containing material in a battery of diffusers and dehydrating the product.

With a more than sufficient supply of raw material demonstrated, and the cost of the furfural set at an arbitrary and safe value of \$0.05 a pound, we are now ready to examine the cost of the process from this point on. The following diagram reveals the quantities of materials involved in producing 100,000 tons of piperylene.



A rough estimate of the cost of the final rubber per pound may be summed up as follows:

Cost of the furfural . . . . .	\$40,800,000
Cost of the hydrogen . . . . . (@ 50¢/1000 cu.ft.)	5,564,000
Estimated cost of operations . . . . .	<u>30,000,000</u>
Total	\$76,364,000
Cost per pound	0.38

Besides piperylene, there would be appreciable amounts (70,000 tons) of marketable by-products from the sylvan hydrogenation alone, which would lower the cost of the pentadiene considerably. At \$0.40 per pound, the price compares favorably with prices of other synthetic rubbers, which ranged from \$0.35 for butyl rubber to \$0.65 for neoprene before March 8, 1943. These prices were superseded at that date by \$0.33 and \$0.45 respectively (11).

#### A. The Hydrogenation of Furfural to Sylvan

Sylvan (2-methyl furan) and tetrahydrosylvan were two of the earliest-reported products of the hydrogenation of furfural (1). However, in this and every other examined instance, they are accompanied by other products which are usually in greater proportion. Table I is a summary of the reported occurrences of these compounds in the hydrogenation products of furfural, furfuryl alcohol, and tetrahydrofurfuryl alcohol.

Table I. Reported Occurrences of Sylvan and Tetrahydro-sylvan in the Hydrogenation Products of Furfural, Furfuryl Alcohol, and Tetrahydrofurfuryl Alcohol.

Compound	Catalyst	Temperature (°C)	Pressure (atmos.)	Time (hr.)	Products	Reference
Furfuryl alcohol	Ni	300	13 hr.	90	Tetrahydrofurfuryl alcohol Tetrahydrofuran Tetrahydro-sylvan	(5)
Furfural	Ni	160	6 hr.	100	Furfuryl alcohol, Furan, Sylvan	(5)
Furfuryl alcohol	Cu-Cr	175	11.5 hr.	100-150	Amyl alcohol - 10% Tetrahydrofurfuryl alcohol and Tetrahydro-sylvan - some. Pentanedioles - 70%	(2)
Furfuryl alcohol	Cu-Cr	250	4 hr.	175	Sylvan - 36% n-Amyl alcohol - 36% Tetrahydrofurfuryl alcohol - 13% Pentanedioles - 29%	(4)
Furfuryl alcohol	Cu-Cr	250	57 hr.	175	Sylvan - 20% Tetrahydrofurfuryl alcohol - 17% Pentanedioles - 30%	(4)
Tetrahydro-furfuryl alcohol	Ni	300	8 hr.	30	Tetrahydrofuran Tetrahydro-sylvan n-Butyl alcohol	(5)
Tetrahydro-furfuryl alcohol	Cu-Cr	250	11 hr.	175	Tetrahydro-sylvan - H <sub>2</sub> O - 5% Tetrahydrofurfuryl alcohol - 70% Pentanedioles - 13%	(4)

(Continued)

Table I (Continued).

Compound	: Cata- : lyst	: Temperature: : (°C) -time:	: Pressure: : (atmos.):	Products	: Refer- : ence
<u>Liquid Phase</u>					
Furfuryl alcohol	Ra- Ni	150 - 4.5 hr.	?	Furfural - 19% Furan - 29% Sylvan - 28%	(15)
<u>Vapor Phase</u>					
Furfural	Ni	270	1	Sylvan, Tetrahydrosylvan, Furfuryl alcohol, Tetrahydrofurfuryl alcohol, etc.	(1)
Furfural	Fe	200	1	Furan, Sylvan, and others	(13)
Furfuryl alcohol	Ni	190	1	Sylvan, Tetrahydrosylvan, Pentanol-2, Pentanone-2.	(1)
Furfural	Cu	175-275	1	Furfuryl alcohol - 4-5% Sylvan - in smaller amounts.	(14)
	Ni	175-275	1	Furfuryl alcohol - 4-5% Sylvan - in smaller amounts.	(14)
Furfural	Cu	160-200	1	Furfuryl alcohol, plus a smaller amount of Sylvan	(12)

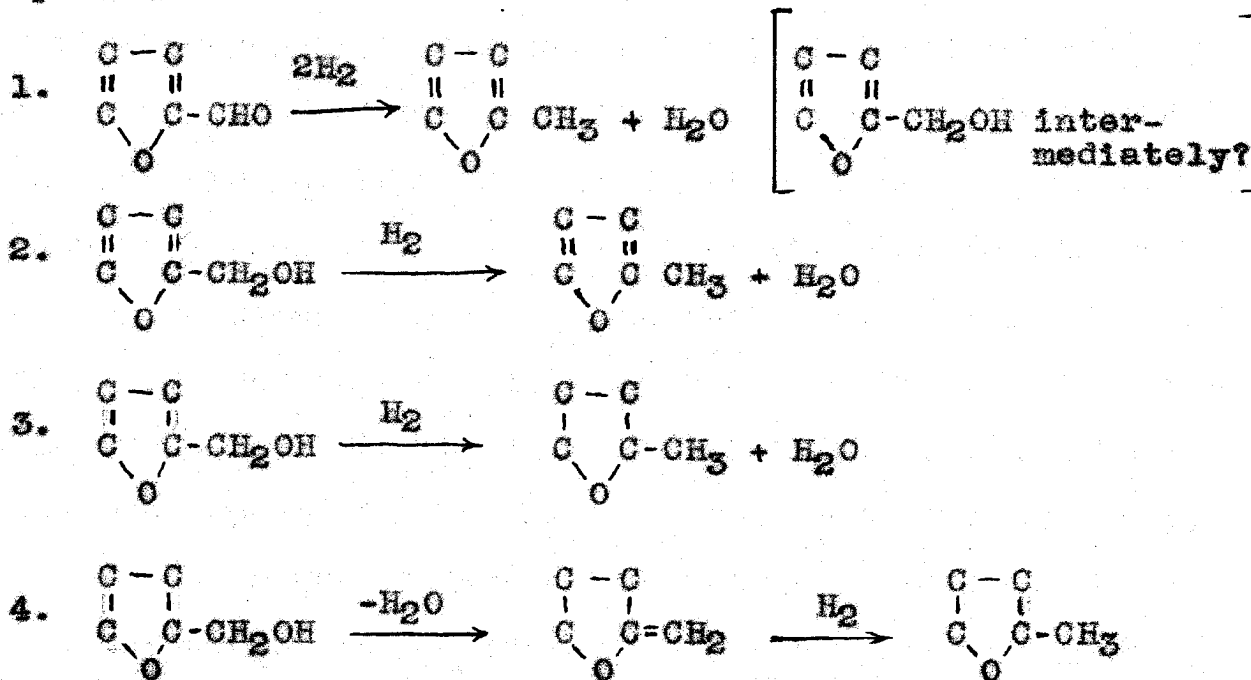
With regard to the last catalyst on the list, the patent (12) describes a continuous vapor phase process for reducing furfural to furfuryl alcohol and sylvan, the latter being formed in about 10% of the amount of furfuryl alcohol. The yield of the alcohol was not given. By repeatedly passing all the alcohol and unchanged furfural over the copper catalyst it was claimed that eventually a near-theoretical yield could be obtained. The copper catalyst was described as being prepared by the reduction of  $\text{CuO}$  between  $140^{\circ}$  and  $200^{\circ}$ . The method of preparation was noted as a factor in its efficacy, but no details were given. Trials in this laboratory to satisfactorily prepare sylvan with  $\text{CuO}$  catalysts prepared in a variety of ways met with little success. As is shown in the experimental part, the yields were not very high. This is not in discordance with the patent.

Brown, Gilman and Van Peurseem (14), in using Ni and Cu catalysts for the vapor phase hydrogenation of furfural, found furfuryl alcohol to the extent of only 4 to 5% and sylvan in even smaller quantities. The temperature range studied was between  $175^{\circ}$  and  $275^{\circ}$ . The copper catalyst was prepared by reducing  $\text{Cu}(\text{OH})_2$  precipitated from the sulfate, and the Ni catalyst by reducing  $\text{Ni}(\text{OH})_2$  precipitated from the carbonate dissolved in nitric acid.

The following four reactions were considered in the development of the present studies. A catalyst was sought which, besides giving just sylvan or tetrahydrosylvan as the



end-product, would produce a high yield in one passage in the vapor phase.

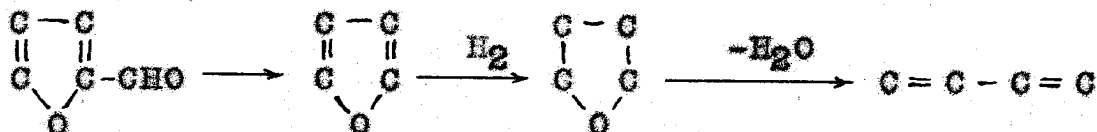


For the starting material, furfural is the cheapest and most desirable, with furfuryl alcohol and tetrahydrofurfuryl alcohol as second and third alternatives since they can be formed easily and almost quantitatively from furfural.

In the case of all the catalysts tried, furfuryl alcohol did not tend to give better yields of sylvan than furfural, thus eliminating the use of this more expensive starting material.

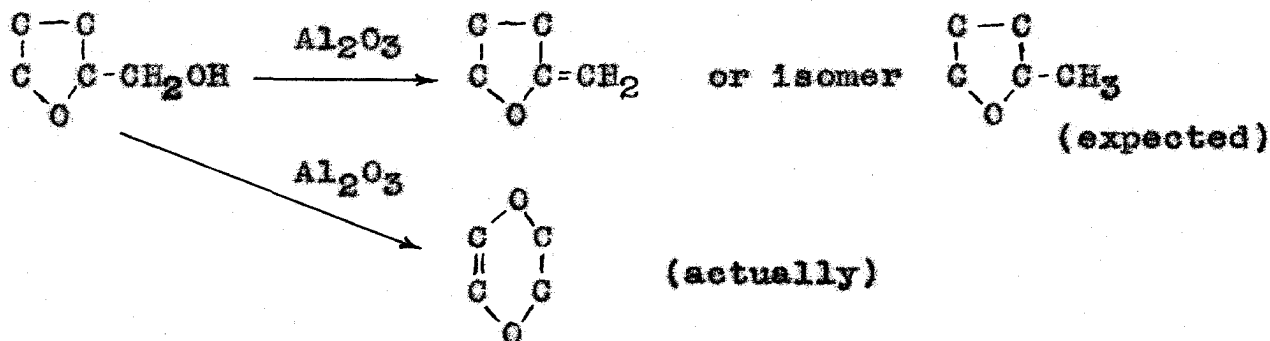
The earliest attempts with alumina as a carrier for various nickel and copper catalysts indicated that the alumina was unsatisfactory, leading to the decomposition of furfural and furfuryl alcohol to furan. This suggests an interesting revision of the original scheme, securing butadiene instead of

piperylene as the end product.



This would probably excite more interest than the development of a piperylene product, since butadiene is the established and accepted source of synthetic rubber. The first reaction indicated is the only one needing development to make the process feasible. The dehydration would be more simple and economical since the number of possible products is reduced. Another approach to the production of butadiene was discovered in the production of considerable tetrahydrofuran during the liquid phase hydrogenation of tetrahydrofurfuryl alcohol with a nickel catalyst.

In the case of reaction four, alumina, especially at high temperatures, was shown to dehydrate the alcohol in an unexpected manner to dihydropyran.



This observation was confirmed by a subsequently found article by R. Paul (16). Attempts to avoid this rearrangement by combining the dehydration and hydrogenation failed.

Copper catalysts formed from the nitrate were observed to be ineffective due to the presence of occluded nitrates. On reducing the catalysts in a hydrogen stream, a strong odor of ammonia was observed, and in every case this was accompanied by ineffectiveness of the catalyst. Repeated washing of the catalysts during preparation does not remove the nitrates with certainty. The sulfate and chloride as sources of a copper catalyst were eliminated due to similar observations in the literature.

By decomposing copper acetate suspended on charcoal in a hydrogen stream at 240° to 260°, a catalyst was found which gave yields of the order of 75% in the conversion of furfural to sylvan. By analogy, it was thought that copper formate would produce a catalyst at least as efficient. Trials with this, however, indicated no hydrogenation at all.

A definitely superior catalyst to the copper acetate was found in copper chromite. It consistently gives yields of over 80%, and a yield of 95% of sylvan has been attained in one passage. It is longer-lived and more easily and effectively regenerated than any of the copper catalysts studied.

It is interesting to notice that in the liquid phase, copper chromite gives chiefly furfuryl alcohol, and sylvan in only small amounts, if any. Calingaert and Edgar (17) use this catalyst to prepare very pure furfuryl alcohol at 50-100 atmospheres and 175-200° in the liquid phase. Adkins and Connor (18) report the same quantitative yield with a pressure

of 100-150 atmospheres and a temperature of 150°. At 175° a 70% yield of pentanediols was observed.

The only carrier tried which gave satisfactory results was activated charcoal. This would give some trouble in regeneration of the catalyst by pumping air or oxygen through at an elevated temperature.

A catalyst which could produce sylvan from furfural as efficiently on a commercial scale as the above two catalysts do on a laboratory scale would make the compound available at a cost of around 13 cents a pound (estimated in the same manner as in part I). At this price, many uses might be devised for it.

The aforementioned patent (12) suggests its use as a motor fuel. This suggestion is dampened somewhat in a paper by Boyan and Beati (19) who recently studied furfural and its derivatives with respect to their use as motor fuels. Furfural, furfuryl alcohol and tetrahydrofurfuryl alcohol, with octane numbers of 53, 83, and 74 respectively, are not suitable because of their ready polymerizability and low volatility. Sylvan, with an octane number of 82.5, is also eliminated because of its polymerizability. Tetrahydrosylvan (octane number, 74) has good volatility, is not easily polymerized, and was the only suitable one studied.

## B. The Hydrogenation of Sylan to Tetrahydrosylan

The hydrogenation of methylfuran has resulted in the formation of several different products also, and a catalyst was sought which effects only the desired ring-saturation with no subsequent ring-splitting.

Table II is a summary of some of the previously reported hydrogenations of the furan ring in compounds of this type.

The ideal, although economically impractical, catalyst already seems to have been found by Zelinsky and Shuiken (20) in osmium, which effects a nearly quantitative conversion in one passage. Shuiken and his co-workers, who have notably been most interested in this reaction (and the process in general), have declared that nickel catalysts are inclined to open the ring and that copper catalysts are unsuitable. They later reported that a catalyst resembling Raney nickel (27% Ni plus 73% Al activated with 10% NaOH) hydrogenated the ring smoothly and showed little sign of fatigue (21).

The patent covering the conversion of furfural to piperylene (6) suggests a nickel catalyst which yields 85% of tetrahydrosylan along with small amounts of pentanone-2 and pentanol-2. Using nickel catalysts prepared in various ways, yields of the order of only 50% have been attained in this

Table II. Reported Hydrogenations of the Furan Nucleus in Furan and Sylvan.

Com- pound	Cata- lyst	Phase (Vapor, Liquid)	Temper- ature (°C)	Pres- sure (atm.)	Product	Ref- er- ence
Furan	Ni	V	170	1	Tetrahydrofuran, - 12% Furan - 34% Butyl alcohol - 8%	(22)
Sylvan	Ni	L	250 2 hrs.	175	Tetrahydro- sylvan - 83% Sylvan - 6%	(4)
Sylvan	Cu- Cr	L	250 4 hrs.	175	Tetrahydro- sylvan - 15% n-Pentane - 5% Pentanol-1 and -2 - 63%	(4)
Sylvan	Os	V		1	Tetrahydro- sylvan quantitatively	(20)
Furan	Os	V	65	1	Tetrahydro- sylvan quantitatively	(21)
Sylvan	Pd	V	160	1	"Hydrogenates smoothly" to tetrahydro- sylvan	(24)
Sylvan	Al- Ni	V		1	Ditto	(21)
Sylvan	Ni	V	120	1	Tetrahydro- sylvan - 85%	(6)

laboratory. With recirculation of the unchanged sylvan 85% conversion could be approached.

In the course of this study, Raney nickel was tried as a catalyst. It was found to be too active in its usual form, resulting in hydrogenolysis. Raney nickel catalysts activated with only 6-8% of the NaOH usually used were shown to be less inclined to cleave the ring, with a consequent rise in the amount of tetrahydrosylvan produced. Yields of around 50% were obtained in one passage. It is suggested that partially activated Raney nickel catalysts may find other useful applications in hydrogenations where the completely activated form results in undesirable decomposition.

Since copper acetate formed an active copper catalyst for the formation of sylvan, it was thought that the nickel resulting from the decomposition of nickel acetate was worthy of investigation with respect to the hydrogenation of sylvan. A trial with a catalyst of this type showed that it possessed some catalytic power but was not as active as certain of the other nickel catalysts studied.

Although vapor phase reactions were desirable for this process, the liquid phase hydrogenation of sylvan, such as that reported by Connor and Adkins (4), which resulted in an 83% conversion to the tetrahydro product, held promise of yielding better results than did the vapor phase hydrogenation. Using the same catalyst as Connor and Adkins, a slightly lower initial pressure (155 atmospheres)

and a temperature of 240-260°, a yield of 68% of tetrahydro-sylvan was obtained, the rest of the product being higher-boiling compounds. This was the best yield observed in all the catalysts studied in either the liquid or vapor phase. A satisfactory catalyst for the vapor phase hydrogenation, such as Os is claimed to be, has not as yet been uncovered in these studies.

### C. Dehydration of Tetrahydro-sylvan

Piperylene, or 1,3-pentadiene, is isomeric with isoprene, the fundamental unit in natural rubber. It also has a conjugated double bond system, a qualification necessary for polymerization. Its polymerizability was first observed by Thiele in 1901 (25), and since then a limited amount of research has been conducted, most notably, again, in Russia, in regard to its polymerization and the properties of the resultant rubber.

One of the first detailed studies of this hydrocarbon and its polymerization products was made by Harries in 1912 (26). The diene was prepared by Grignarding acrolein and dehydrating the resulting carbinol, or by debrominating 2,3-amylene bromide (from ethyl formate and magnesium ethyl bromide) by means of soda lime. It was polymerized in two manners: with sodium, and by long heating (14 days at 105°). The product was then used in comparative studies with other



synthetic polymers.

Other methods of preparing this hydrocarbon were devised by Kyriakides (27). By passing 2,4-pentanediol over aluminum phosphate at 450° and 35 mm., or by passing pentene-2,ol-4 over kaolin at 400-420° and 60-75 mm., near-theoretical conversion to piperylene was secured. Another "wet" method consisted in dehydrating 2,4-pentanediol, using HBr as the catalyst. By this method, 50% yields were obtained.

Reppe, Steinhofer and Hecht (28) have been granted a patent for the conversion of tetrahydrofuran and its homologs to butadiene (and its homologs) by passing the compound over a phosphate dehydration catalyst. Another patent (5), the one including the entire furfural to piperylene process, covers the same reaction applied specifically to tetrahydro-methylfuran. It is claimed in this patent that yields of the order of 85-90% may be obtained over the usual catalysts used for the dehydration of alcohols, such as alumina and kaolin.

Trials with several different dehydration catalysts of the types mentioned in both patents have indicated either that their yields have been grossly exaggerated or that the effective catalyst was too subtly mentioned - a not unknown occurrence.

With the catalysts tried, the small amount of 1,3-pentadiene formed was accompanied by a comparable quantity of a lower-boiling fraction presumably consisting chiefly of its 1,4 isomer boiling at 25°. This is not an unexpected

occurrence, but its absence in the reaction products described in the latter patent is a source of speculation. The solution may be found in the untried catalysts mentioned in the patents.

Two other approaches, hitherto unreported, were suggested by analogous studies found in the literature. One was suggested by Henne and Turk (29) in their paper on the formation of conjugated diolefins by double bond displacement. Their experiments involved the shifting of two double bonds from their unconjugated positions to a conjugated form, as, for example, the isomerism of 1,5-- to 2,4-hexadiene. This was accomplished over activated alumina at temperatures around 365°. All the compounds studied involved the shifting of two bonds and were composed, consequently, of six carbon atoms or more.

If applied to 1,4-pentadiene, the same displacement to a conjugated system would be expected to occur. Since this involves the shifting of only one double bond instead of two, the change might be more completely effected. In the example given above (the compound studied that was most similar to 1,4-pentadiene) the yield in one passage was 39% of the 2,4-hexadiene. With more than one passage over the alumina, much more quantitative yields would be expected. Since in the catalysts studied the 1,4-pentadiene fraction was as large, on an average, as the piperylene fraction, its isomerization

would appreciably increase the eventual yield of the desired conjugated compound.

Not enough of the 1,4-pentadiene fraction was collected to try this.

Another method of dehydrating the tetrahydrosylvan is suggested in the previously-mentioned work of Kyriakides (27), who effected his dehydrations in vacuo. This was resorted to in order to decrease the amount of carbonization occurring on the catalyst at ordinary pressures, this being indicative of a general decomposition to gaseous products, including hydrogen. The presence of trimethylethylene in the product of the dehydration of amylene oxide was attributed to the reduction of isoprene by the hydrogen thus formed. Use of pressures of 60 mm. and less greatly increased the yield and reduced charring. This effect was observed earlier by Staudinger and Klever (30) in the formation of isoprene from terpene hydrocarbons.

In the application of this refinement to the dehydration of tetrahydrosylvan, it was thought that formation of the considerable amount of higher-boiling compounds could be minimized, resulting in a higher yield of the pentadiene. This was found to be the case. Besides reducing charring, reducing the amount of higher-boiling compounds and increasing the amount of piperylene formed, less of the 1,4-pentadiene fraction was received.

A literature survey shows that the polymerization of

piperylene to a synthetic rubber has been accomplished with the same catalysts and by the same methods as those used in the preparation of the usual types of synthetic rubbers. Besides the sodium and heat methods reported by Harries (see page 18), Mark and Raff (31) have listed aluminum chloride, stannic chloride and activated clay as effective catalysts for its polymerization. Emulsion polymerization, a recently popularized method, has yielded a very satisfactory rubber in this laboratory. Although the polymerization of the piperylene is outside the scope of the present study, it was undertaken as a means of further derivatizing the piperylene received.

## II. EXPERIMENTAL PART

### A. Description of Apparatus

Due to the volatility of the expected products and the amount of unused hydrogen involved, a closed-circuit recirculating hydrogenator was considered to be most desirable.

The essential parts of the apparatus used, as shown in diagram I, are: A, a hydrogen reservoir of 17-liter capacity; B, a vaporizing flask (125 cc.) sealed by means of a short connecting tube to C, the pyrex catalyst tube, 45 cm. in length and with a capacity of 400 cc. of catalyst. The vaporizing flask is enclosed in an electrically heated Wood's metal bath and the catalyst chamber is surrounded by an electrically heated and controlled, well-insulated furnace, N. D and F are two condensers (50 cc. bulbs), the first ice-cooled and the second cooled with an acetone-dry ice mixture; both are set in thermos containers, P. The  $\text{CaCl}_2$  drier, E, is to prevent the formation of ice in the glass coils of the second condenser. The diaphragm pump, G, is run by a 300 r.p.m. constant-speed motor and the recirculation regulated by a screw clamp in the gas line. The flowmeter, H, is to indicate the rate at which hydrogen is being used up. They are calibrated in cc./min.

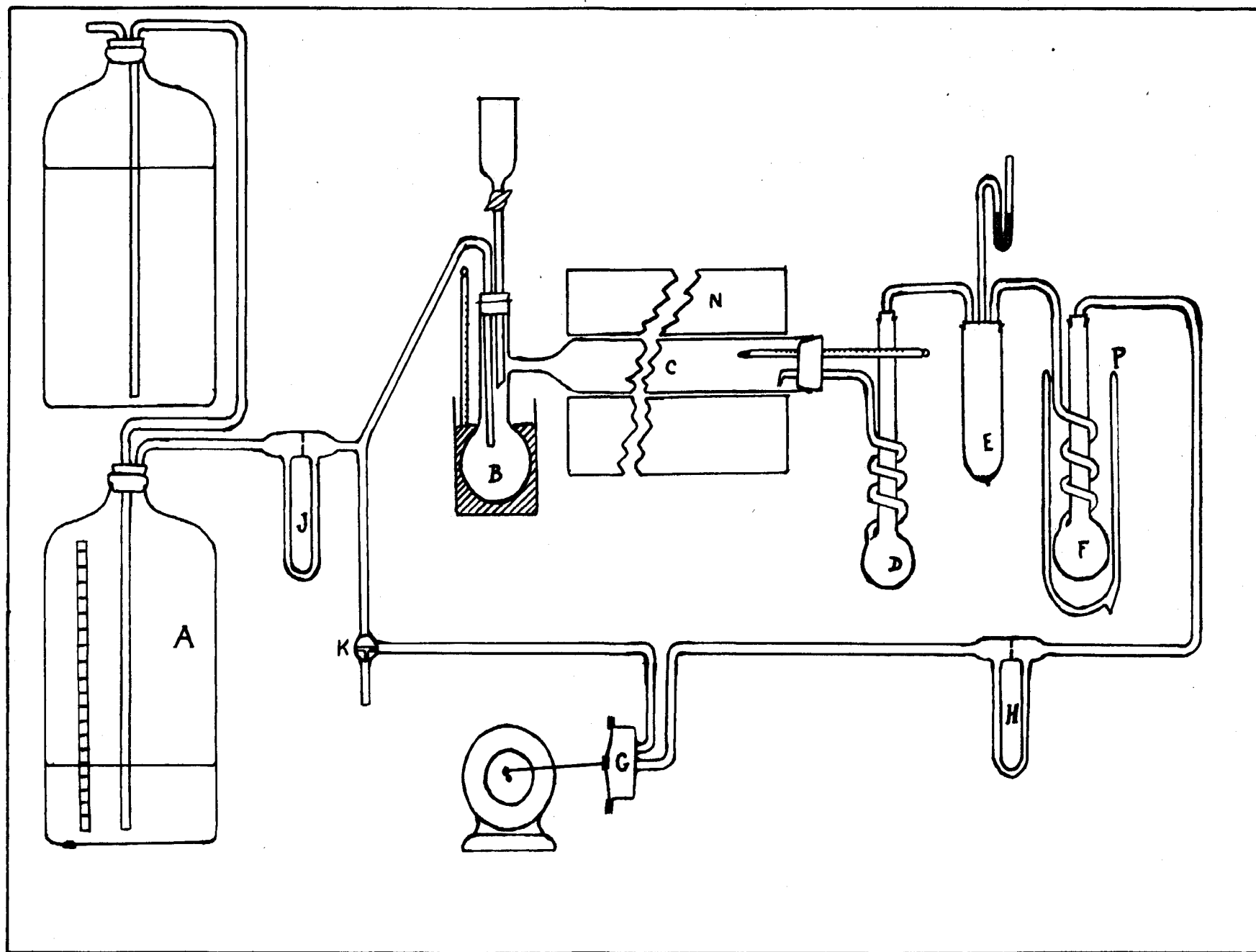


Fig. 1 Hydrogenation Apparatus

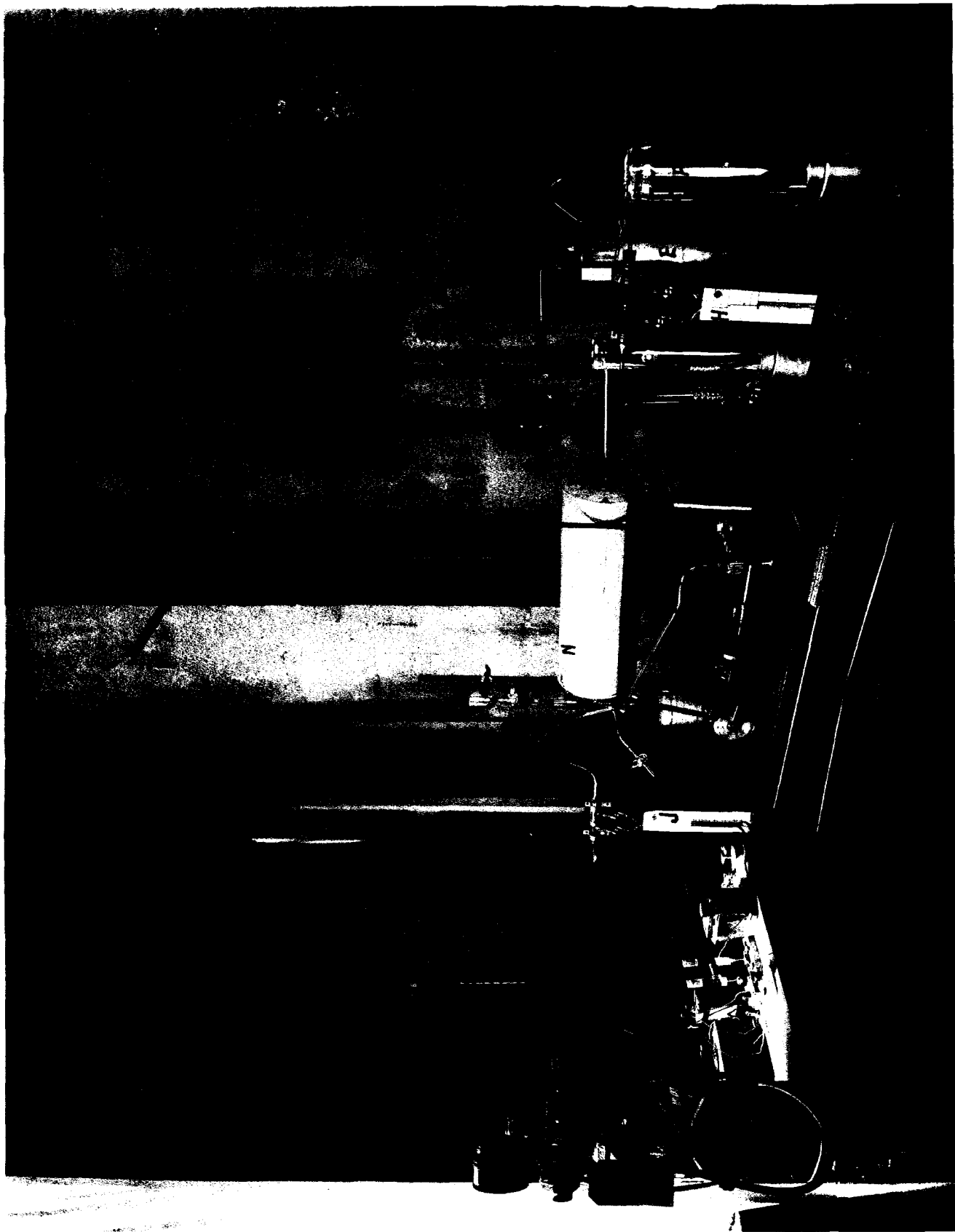


Fig. 2. Hydrogenation Apparatus

The vaporizing flask temperature and the furnace temperature are regulated by means of transformers and the temperatures are measured by a thermometer in the metal bath and a thermometer in the catalyst mass. In addition to this, the apparatus used had three thermocouples fastened to the ends and middle of the aluminum furnace tube through which the glass catalyst chamber passed. The thermometer in the catalyst mass is then not necessary - and not practical if the temperature is much above  $360^{\circ}$ , as in the dehydration operations.

X In use, the apparatus is flushed out with hydrogen with stopcock K in the position shown in the diagram. With the vent closed by adjusting K, the pump is then started and the circulation is adjusted to the desired rate (usually the maximum) by means of a screw clamp in the line between H and G. With a constant metal bath temperature, below the boiling point of the compound, and a constant recirculation rate, the efficacy of various catalysts can then be compared, during the process by flowmeter J, and after the process by analysis of the products in the condensers.

The effect of temperature on the efficiency of a catalyst can be observed by varying the temperature during a run and observing the difference in the rate at which hydrogen is being used up as measured by flowmeter J. The best vaporizing flask temperature would, of course, depend on the maximum rate at which the substance can be sent through and



still be efficiently hydrogenated.

By using a water bath or no bath at all around the vaporizing flask, the apparatus is adapted for the lower-boiling liquids such as sylvan and tetrahydrosylvan. With nitrogen or some other inert gas in place of  $H_2$ , the apparatus is suitable for vapor phase dehydrations, but in this case the process cannot be followed with flowmeter J, since no gas is being used up.

#### B. Fractionation of Products and Calculation of Yields

For the separation of the products of the hydrogenations and dehydrations, a 50 cc. distilling flask was fitted with a side neck 14 mm. in diameter and 20 cm. in length, the side arm to the sealed-on condenser being 4 cm. from the top. This neck was filled to a height of 11 cm. with small glass helices of an average of one turn.

Although the separation of sylvan from the products of hydrogenation of furfural presented no problem because of the difference in boiling points of the compounds involved, the separation of sylvan and tetrahydrosylvan offered difficulties. Their difference in boiling points is  $15^\circ$ , and a mixture of the two boils chiefly in an intermediate range. Arbitrarily, in distilling a mixture of the two, the fraction

boiling below 75° was considered the unchanged sylvan and that fraction boiling between 75° and 85° was considered as tetrahydro-sylvan.

Two different methods were used in calculating yields. The yield could be based on (1) the amount of starting material or (2) on the amount of product received. Since there was an appreciable loss of material in its passage through the catalyst, the yield based on the latter method was, as a rule, considerably higher. In the hydrogenation of furfural, for example, 50 gm. of furfural might be placed in the vaporizing flask and only 35 gm. of product be found in the receivers. If the 35 gm. of product included 25 gm. of sylvan, the yield calculated on the basis of amount of furfural introduced would be:

$$\frac{25 \times 96}{50 \times 82} \times 100 = 58.6\%$$

On the basis of amount of product received (neglecting added weight of hydrogen taken up) the yield would be:

$$\frac{25 \times 96}{35 \times 82} \times 100 = 83.6\%$$

Loss of this much material was common in the first passage of furfural through the catalyst, but in subsequent passages the loss was more commonly of the order of 1 to 5 gm.

The method used in calculating the yields is specified in each instance in the following experiments.

### C. Action of Nickel and Alumina Catalysts on Furfural and Tetrahydrofurfuryl Alcohol

For these experiments, an apparatus with a smaller catalyst chamber and no recirculating device was used, and the compound was vaporized by bubbling hydrogen through the heated liquid or by dropping the liquid into the vaporizing flask, which was heated above the boiling point of the compound.

Although the exit gases passed through a dry ice-acetone-cooled receiver as well as an ice-cooled one, much product was lost in the escaping hydrogen.

#### 1. Hydrogenation of furfural with a nickel catalyst

Twenty-seven grams of nickel nitrate hexahydrate were dissolved in distilled water and a solution containing 18 gm. NaOH was added to precipitate  $\text{Ni}(\text{OH})_2$ . The precipitate was washed by decantation 5 times, then in a Buchner funnel with two portions of water. The cake was re-suspended in water and asbestos was added. The resultant mass was filtered, washed twice, pressed as dry as possible, and dried at  $100^\circ$  over night.

The catalyst was loosely packed in the catalyst chamber and reduced in a stream of hydrogen at  $250-300^\circ$ , leaving black and finely divided metallic nickel on the asbestos carrier.

With the catalyst mass at a temperature of  $290^{\circ}$ , 25 gm. of furfural were introduced into the flask heated by an oil bath to  $110^{\circ}$  and hydrogen was bubbled through at a rate of 50-60 cc. per minute. It was run until 7 gm. were left in the vaporizing flask.

In the ice-cooled receiver were 3 ml. of a mixture consisting chiefly of furfural and water.

In the dry ice-acetone-cooled receiver were 4-5 cc. of a clear volatile liquid containing white ice flakes. A warm water bath distilled over 5.4 gm. between  $31^{\circ}$  and  $35^{\circ}$ , leaving a slight amount of yellow residue. On drying and redistilling, the following constants were obtained:

B. Pt. --  $31-32^{\circ}$   
n<sup>21</sup> -- 1.420  
d<sup>21</sup> -- 0.9133  
21

These constants correspond to those of furan, which are:

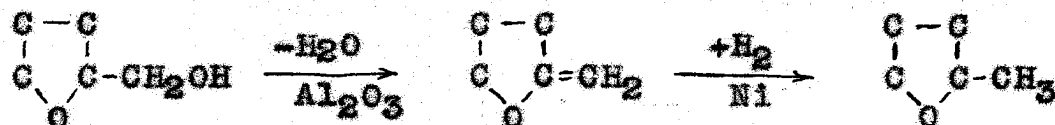
B. Pt. --  $31.4^{\circ}$   
n<sup>21</sup> -- 1.4215  
d<sup>21</sup> -- 0.9366  
21

The formation of furan indicates that hydrogenolysis, rather than a simple hydrogenation, occurred. Based on the amount of furan caught and the amount of furfural used up, a

yield of 42.5% was obtained. Repetition of the experiment with new catalysts and at temperatures up to 350° yielded the same product in varying amounts.

2. Hydrogenation of tetrahydrofurfuryl alcohol with Ni on alumina

With both a dehydrating catalyst and a hydrogenation catalyst, the following reaction was considered possible:



Small lumps of activated alumina were impregnated with Ni(OH)<sub>2</sub>, dried and reduced at 300° in a stream of hydrogen. With the catalyst at 300°, 54 gm. of tetrahydrofurfuryl alcohol was passed through in 45 hours. The hydrogen rate was 130 cc./min.

Distillation of products in first receiver

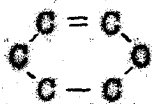
Below 100°	--	1.5 ml.
100-110°	--	5.0 ml.
173-180°	--	16.0 ml.
Residue	--	<u>2.0 ml.</u>
		24.5 ml.

Distillation of products in second receiver

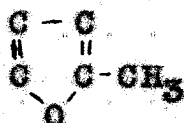
68-88°	--	5.0 ml.
88-100°	--	5.0 ml.
100°	--	<u>16.0 ml.</u>
		26.0 ml.

Total product = 24.5 ml. + 26.0 ml. = 50.5 ml.

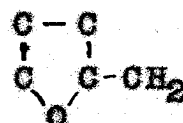
This procedure was repeated three times and the product boiling below 100° was collected, dried and distilled. The major portion boiled between 81° and 86°. It was considered to be one of the following three compounds:



B. Pt. 86-87°



B. Pt. 86-87°



B. Pt. 82-83°

To characterize it, it was placed in a microhydrogenation apparatus with a PtO catalyst. The rate of hydrogenation was very rapid, but frequent additions of catalyst were needed. The hydrogenation should have required, theoretically, 2900 cc. of hydrogen. Actually, 2110 cc. were absorbed. Most of the product distilled between 85° and 87°, and the following constants were observed for this fraction. The corresponding data for tetrahydropyran and tetrahydro-sylvan are included for comparison.

	<u>Product</u>	<u>Tetrahydro- pyran</u>	<u>Tetrahydro- sylvan</u>
B. Pt.	85-87°	86-87°	78-79°
$n_D^{21}$	1.4228	1.42215	1.4059
$d$	.8341 <sup>17</sup>	.834	.8534

This indicates that the product of the tetrahydrofurfuryl alcohol reaction is dihydropyran rather than the desired tetrahydro-sylvan.

### 3. Hydrogenation of tetrahydrofurfuryl alcohol in the liquid phase

Using the same kind of nickel on alumina catalyst as before, a charge of tetrahydrofurfuryl alcohol was placed in the bomb of a Parr high pressure hydrogenator and reduced for 2 to 3 hours at 200°.

By warming the product in a water bath, 11.4 grams of a clear, volatile liquid distilled below 75°. After drying this portion, it was refractionated and found to boil between 62° and 64°, with the principal boiling point at 64°. Its refractive index and density were determined and found to agree most favorably with these of tetrahydrofuran.

	<u>Product</u>	<u>Tetrahydrofuran</u>
B. Pt.	64°	64-65°
n	1.4048 <sup>22</sup>	1.407
d	.891 <sup>22</sup>	.888 <sup>21</sup>

The rest of the product, boiling above the temperature of the water bath, was not examined.

### D. Hydrogenation of Furfural to Sylvan

In these experiments, the apparatus diagrammed and described on pages 23 to 27 was used. The technical grade furfural used was distilled to remove the tarry black residue.

### CATALYST NO. 1

Copper hydroxide was precipitated from copper nitrate and NaOH, filtered on a Buchner funnel and washed. Three compact rolls of copper screen were dipped into a sludge of the precipitate, placed in the catalyst chamber, and dried and reduced at 250° to metallic copper.

With the catalyst at 210° and the bath at 110°, 50 gm. of furfural was passed through the catalyst in 6-1/2 hours.

The water-clear product in the second receiver (14.5 gm.) distilled completely between 61° and 64°, with the major portion boiling at 63°.

#### Physical constants:

	<u>Product</u>	<u>Sylvan</u>
B. Pt.	63°	62-63°
n	1.4324 <sup>20</sup>	1.433 <sup>21-22</sup>
d	.914 <sup>20</sup> <sub>20</sub>	.916

The compound was further characterized by forming the 5-methyl-2-chloromercurifuran according to the directions of Gilman and Wright (32). Its melting point was 130°.

A small amount of sylvan was distilled from the furfural-water mixture in the first receiver, bringing the total amount of sylvan formed to 16 gm. The yield based on 50 gm. of furfural was 37.5%.

On passing 50 gm. more furfural through the catalyst at a temperature of 250°, 14.0 gm. of sylvan was formed. Air was blown through the catalyst kept at a temperature of 200° in an



attempt to reactivate it. Fifty grams of furfural passed through it after this treatment yielded 8.5 gm. of sylvan.

The above experiments were performed with conditions simulating those described in the patent (12). The yield of sylvan was greater than that claimed in the patent. The catalyst did not seem to be restored to an appreciable degree by oxidation and subsequent reduction as the patent suggests.

#### CATALYST NO. 2

One hundred grams of activated charcoal lumps were added to a solution of 100 gm. of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Cu}(\text{OH})_2$  was precipitated by the addition of a solution containing 25 gm. of KOH. The mixture was washed 5 times in a Buchner funnel with boiling water, placed in the catalyst chamber and reduced at  $210^\circ$  to metallic copper in a stream of hydrogen.

At a furnace temperature of  $200^\circ$  and a bath temperature of  $120^\circ$ , 95 gm. of furfural were sent through the catalyst. Of the 83 gm. of product in the two receivers, 53 gm. was sylvan. On the basis of the weight of product, the yield of sylvan was 75%.

A subsequent run with the same catalyst gave an 88% conversion based on the weight of product received.

Four later attempts to duplicate this catalyst were unsuccessful. In the reduction of the catalyst in each of these instances, the exit gases smelled strongly of ammonia and turned moist red litmus blue. This is due most probably

to the reduction of nitrates present from the precipitation, and repeated washing failed to remove them. The inefficiency of the catalysts was attributed to their presence and no explanation is forthcoming for the efficiency of the first catalyst prepared in this manner.

#### CATALYST NO. 3

A hot saturated solution of  $\text{Cu}(\text{OAc})_2$  was poured over 100 gm. of activated charcoal lumps (Norite A); the mixture was stirred and the liquid drained off. After the charcoal was nearly dry, this operation was repeated. On drying, the charcoal was well covered with blue-green crystals of copper acetate. It was placed in the catalyst chamber, dried and decomposed at  $250^\circ$  overnight in a stream of hydrogen.

At a furnace temperature of  $210-220^\circ$  and a bath temperature of  $130^\circ$ , 100 gm. of furfural was run through in two 50-gram batches. The rate of hydrogenation was much higher than it had ever been. The yield of sylvan based on the weight of product received was 68.6%. A later run of 50 gm. of furfural gave an 80% yield of sylvan. This catalyst has been made several times and always was efficient in effecting the conversion of furfural to sylvan. No study has been made on its regeneration.

#### CATALYST NO. 4

Lumps of coke were substituted for the activated charcoal in the procedure for catalyst #3. No hydrogenation occurred over this catalyst.

#### CATALYST NO. 5

Suspecting the activated charcoal of possessing some catalytic power, a charge of furfural was passed over it at 200°. No hydrogenation occurred.

#### CATALYST NO. 6

Powdered activated charcoal (Norite A) was added to a hot saturated copper acetate solution. Lumps of coke were next added; the solution was boiled a few minutes and filtered on a Buchner funnel.

The above catalyst was reduced at temperatures up to 325° in a stream of hydrogen in the catalyst tube. With a furnace temperature of 210°, 50 gm. of furfural were passed through. The hydrogenation rate was very low and only a trace of sylvan was found in the product.

#### CATALYST NO. 7

One hundred grams of activated charcoal lumps was soaked in a solution containing 50 gm. of copper acetate and 5 gm. of chromic acetate. This process was repeated; the catalyst was dried, placed in the catalyst chamber and reduced at 240-260°.

At a furnace temperature of 220° and a bath temperature of 130°, 100 gm. of furfural was passed through. The rate of hydrogenation was almost as high as that with catalyst #3, and the yield of sylvan was 40-50%.

#### CATALYST NO. 8

The same procedure as that followed in making catalyst

#7 was used, substituting cadmium acetate for chromic acetate. No hydrogen at all was taken up.

#### CATALYST NO. 9

Wood charcoal sticks (General Chemical Co.) were substituted for the activated charcoal lumps in the procedure for catalyst #3. The reduced catalyst seemed to have much more copper on the surface than catalyst #3, but the hydrogenation rate was very low, and there were only traces of sylvan in the product.

#### CATALYST NO. 10

Copper oxide wire sticks were placed in the catalyst chamber and reduced at 225-325°.

At a furnace temperature of 225° and a bath temperature of 135°, 50 gm. of furfural was passed through. There was an appreciable amount of sylvan formed, but the catalyst did not approach the efficiency of the copper acetate or the copper acetate-chromium acetate catalysts.

#### CATALYST NO. 11

One hundred grams of activated charcoal lumps was added to a hot solution containing 50 gm. of copper acetate. Copper oxide was precipitated on the charcoal by the addition of a solution containing 27 gm. of potassium hydroxide. It was filtered on a Buchner funnel and washed twice with hot water. The catalyst was reduced in a hydrogen stream at 225°.

With a furnace temperature of 250° and a bath temperature

of 130°, 100 gm. of furfural was passed through. The yield of sylvan was 24%, based on the amount of furfural passed through.

#### CATALYST NO. 12

Compact rolls of copper screen were exposed to acetic acid vapors until a coating of copper acetate was formed. They were placed in the catalyst tube and reduced at 250° in a hydrogen stream. Upon passing 40 gm. of furfural through this catalyst, no hydrogenation occurred.

Other methods of coating copper screen and copper turnings with copper acetate were tried, but the resultant catalysts did not effect the hydrogenation.

#### CATALYST NO. 13

Thirty-five grams of ceric oxide was treated with 46 ml. of concentrated sulfuric acid plus 15 ml. water, and heated to boiling for five minutes. The solution was cooled and 450 ml. of water was added. It was then digested for an hour and filtered. There was still considerable oxide undissolved. Sodium hydroxide was added until just alkaline, and the ceric hydroxide was all precipitated. It was washed by centrifuging 6 to 8 times with distilled water. Copper hydroxide was precipitated from copper acetate and sodium hydroxide and washed twice by centrifuging it. The oxides were mixed and 100 gm. of charcoal was coated with the resultant paste. The catalyst was placed in the tube, dried, and reduced in hydrogen at 250°.

The yield of sylvan from the first 50 gm. of furfural passed through this catalyst was 37.4%. This was a higher yield than that received with the plain copper precipitated from copper acetate (catalyst #11).

#### CATALYST NO. 14

Ceric hydroxide was made as in the preparation of catalyst #13, placed on activated charcoal lumps, and dried in hydrogen at 260°. There was no change in the appearance of the yellow ceric hydroxide (oxide) coating. At furnace temperatures of 200-235° no hydrogenation was effected.

#### CATALYST NO. 15

It was thought probable that copper formate, since it is more easily decomposed and leaves a more metallic appearing deposit, would yield at least as efficient a catalyst as copper acetate .

Black copper oxide was precipitated from a hot solution of copper acetate and sodium hydroxide. The precipitate was filtered, washed thoroughly and dissolved in strong formic acid. Copper formate crystallized from the solution and was filtered off, washed with a very small amount of water, and bottled. The mother liquor, saturated with copper formate, was used to soak 100 gm. of lump charcoal. Upon drying after the second treatment with this solution, small crystals of copper formate covered the charcoal.

This catalyst was placed in the catalyst chamber and

decomposed in hydrogen at 200°. No hydrogenation was indicated by the flowmeter while furfural was being passed through, but a few drops of sylvan were found in the second receiver.

#### CATALYST NO. 16

One hundred grams of charcoal was soaked in a hot solution of 35 gm. copper acetate and 5 gm. manganese acetate. After the second such treatment, it was placed in the catalyst tube and reduced at 250°.

With a furnace temperature of 240°, 50 gm. of furfural was run through this catalyst. From the 45 gm. of product received, 9 gm. of sylvan was separated. On the basis of the amount of product, this was a 21% yield.

#### CATALYST NO. 17

A copper acetate catalyst was prepared by shaking together 35 gm. of powdered copper acetate and 100 gm. of wet lump charcoal. After decomposing the catalyst as usual, 50 gm. of furfural was passed through. The hydrogenation rate, as measured by the first flowmeter, was higher than with any other catalyst. The amount of product was 31 gm., of which 17.3 gm. was sylvan, a 65.5% yield, based on the product received.

Besides being as efficacious as the catalyst prepared from a solution of the acetate, catalyst #3, this method of preparation has several advantages: the time involved in preparing it is a small fraction of that for catalyst #3; all the copper is deposited on the outside surface of the charcoal;

the amount of copper on the catalyst is much more easily controlled.

#### CATALYST NO. 18

Thirty-five grams of copper acetate was powdered and mixed with 400 cc. of wet activated alumina lumps (14-30 mesh). This was placed in the catalyst tube and decomposed in hydrogen at a furnace temperature of 250°.

During the hydrogenation of 50 gm. of furfural at a furnace temperature of 210°, 21 liters of hydrogen was taken up. Based on 34.5 gm. of product received, however, only a 44% yield of sylvan was formed. A few drops boiling around 75° and smelling strongly of tetrahydrosylvan were noticed. After the furfural-water mixture was distilled off, boiling around 97-100°, the rest of the product distilled between 160° and 172°, indicating a mixture of furfural and furfuryl alcohol. This does not account for all of the hydrogen used up. The apparatus did not leak.

#### CATALYST NO. 19

A catalyst carrier was prepared from plaster of Paris by squeezing the almost-set plaster through a potato ricer, letting the strings dry, and breaking them into short lengths. Thirty-five grams of powdered copper acetate was mixed with this wet carrier and the catalyst placed in the hydrogenator and decomposed in a stream of hydrogen at 250°.

At a furnace temperature of 200° and a bath temperature



of 130°, 50 gm. of furfural was passed through the catalyst, but no hydrogenation took place.

#### CATALYST NO. 20.

A copper chromite catalyst was prepared according to the directions of Conner, Folkers and Adkins (33). Nine hundred milliliters of a solution (80°) containing 261 gm. copper nitrate trihydrate and 31.3 gm. barium nitrate was added to a solution containing 151.2 gm. ammonium dichromate and 225 ml. of 28% NH<sub>4</sub>OH. The precipitate was filtered on a Buchner funnel, the cake pressed with a spatula and sucked as dry as possible. After drying at 75-80° overnight and pulverizing, the product was decomposed in several portions in a casserole over a free flame. After cooling, it was leached with 600 ml. of 10% HOAc for 30 minutes and then washed with 600 ml. of water in six portions. The dried and pulverized product weighed 161 gm.

Thirty-five grams of this copper chromite catalyst was sprinkled on wet charcoal lumps and dried in the hydrogenator in a stream of hydrogen at 270°.

At a furnace temperature of 200° and a bath temperature of 130°, 50 gm. of furfural was started through the catalyst. The initial rate of hydrogenation was so great that the pumping speed (usually at the maximum of the recirculation flowmeter) had to be reduced to about one-fourth of the maximum to keep the oil in the hydrogenation rate flowmeter from

overflowing. Of the 34.6 gm. of product received, 24.6 gm. was sylvan. Based on the amount of product, the yield was 83.2%. Another 50 gm. of furfural passed through yielded 47.3 gm. of product, 38.5 gm. of which were sylvan. This is a yield of 90.2% on the basis of starting material and a yield of 95.4% on the basis of amount of product received. The next 100 gm. of furfural gave an 81.1% conversion (on the basis of amount of product).

Furfuryl alcohol run through this same used catalyst gave a 67.2% yield on the same basis.

The yield from the final amount of furfural (371 gm.) sent through the catalyst in eight different batches was 64.1%. Based on the 332 gm. of product received, the yield was 71.5%.

Another catalyst prepared in the same way was used to determine the temperature range through which it hydrogenated efficiently. The hydrogenation rate, starting very low at 140°, increased slowly to a maximum between 200° and 230°. The rate was still high around 280°, but fell off noticeably above this temperature. There was still a small amount of hydrogenation at 330°, the highest temperature reached.

When the furnace had cooled to 210°, 25 cc. of furfural was passed through the catalyst. The hydrogenation rate was very low, and not much sylvan was formed. Air was pumped through the catalyst kept at a temperature of 200° for about one-half hour. This treatment increased the rate of hydrogenation appreciably but did not restore the catalyst to its

original activity.

In table III the various catalysts are listed in the approximate order of their efficiencies.

#### E. Use of Large Apparatus for the Hydrogenation of Furfural

An apparatus was constructed which included a counterpart of every feature of the small-sized hydrogenator. The parts in the accompanying photograph are lettered to correspond to those in the diagram on page 24. The furnace was vertical instead of horizontal, and the whole apparatus, with the exception of a few rubber connections added in modifying the machine, was constructed of metal. The catalyst chamber was an iron pipe with thirteen times the volume of the smaller one. The smaller condenser tubing and other piping was of copper. The brass vaporizing flask had a capacity of one liter. The catalyst chamber and vaporizing pot were electrically heated as in the smaller apparatus. Just as was noted in the case of the smaller machine, it is suited for all types of hydrogenations, dehydrations and other vapor phase catalytic reactions.

The catalysts tried in this apparatus for the hydrogenation of furfural included copper hydroxide precipitated from the nitrate on charcoal and reduced to copper, copper turnings

Table III. Catalysts Studied in Approximate  
Order of Efficiency

Catalyst	Number	% Yield of Sylvan
Copper chromite on charcoal	20	Up to 95%
Copper acetate on charcoal	3, 17	Up to 80%
Copper ppt'd from copper nitrate on charcoal	2	75% (not able to duplicate)
Copper acetate and chromium acetate on charcoal	7	40-50%
Copper acetate on alumina	18	44% 70.5%
Copper hydroxide and ceric hydroxide on charcoal	13	37-38%
Copper from copper nitrate on copper screen	1	37.5%
Copper oxide wire sticks	10	
Copper ppt'd from copper acetate and KOH on charcoal	11	24%
Copper acetate and manganese acetate on charcoal	16	21%
Copper acetate on powdered charcoal with coke	6	Very low
Copper acetate on plain wood charcoal	9	Very low
Copper formate on charcoal	15	Very low
Copper acetate on coke	4	No hydrogenation
Activated charcoal lumps	5	" "
Copper acetate and cadmium acetate on charcoal	8	" "
Copper acetate formed on copper screen with HOAc vapors	12	" "
Ceric hydroxide on charcoal	14	" "
Copper acetate on plaster of Paris	19	" "



Fig. 3. Large Hydrogenation Apparatus

oxidized and reduced, copper from copper acetate on charcoal, and copper chromite on charcoal. The last two were the only ones that formed an appreciable amount of sylvan. The copper acetate catalyst was not as effective in this machine as it was in the smaller one. The copper chromite catalyst was the only satisfactory one tried, giving yields comparable to those received in the smaller apparatus. A hydrogenation using this catalyst will be described.

The catalyst was prepared by distributing 340 gm. of copper chromite on 2-1/2 pounds of wet activated charcoal lumps. This was placed in the catalyst chamber and dried overnight at 210° in a slow stream of hydrogen.

With the furnace at 210° and the vaporizing pot at 130°, 400 gm. of furfural was started through the catalyst. Numerous leaks were observed in the solder between the pot and the furnace. The hydrogenation rate, starting out very low, gradually built up to a point where a very satisfactory product was obtained. Twelve hundred grams of furfural was sent through in one day. The next day, after having been left overnight with a small hydrogen stream passing through the machine, 1000 gm. of furfural was passed through. During the next two days, 1200 and 1000 gm., respectively, were sent through, the hydrogenation rate showing a slight improvement, if any change. The next day, the first 200 gm. of furfural was hydrogenated as usual, but subsequent batches came through unchanged. It was noticed that the vaporizing pot

thermometer was apparently broken since no mercury appeared in the visible portion of the stem.

In an attempt to regenerate the catalyst, air was then pumped through it at 200° until most of the exit fumes had disappeared.

On flushing out the apparatus with hydrogen and passing more furfural through the catalyst, no hydrogenation occurred.

An explanation was found for the sudden cessation of the hydrogenation when the pot was detached and found to be full of charcoal. The screen supporting the catalyst had given way, dropping the catalyst into the pot, and it is presumed that this happened at the time the hydrogenation stopped. Since the heat of reaction has raised the furnace temperature (measured in the top of the catalyst) at times to above 300°, it is not unlikely that the bottom of the catalyst mass reached a temperature high enough to melt the solder holding the screen in place.

The following results from this hydrogenation were compiled after distilling the product:

Furfural passed through . . . . .	4600 gm.
Product received . . . . .	3453 "
Material lost . . . . .	1147 "
Sylvan produced . . . . .	1946 "
Water formed (calculated) . . . . .	426 "
Residue from sylvan distillation .	1507 "
Residue minus water . . . . .	1081 "
Yield based on product recovered .	65.2%
Gm. sylvan produced/gm. copper chromite .	5.72

This overall yield of 65.2% compares favorably with the 71% overall yield obtained with the smaller apparatus (see page 44), particularly when it is pointed out that in using ten times the amount of catalyst, more than ten times the amount of product was received and that the catalyst still showed no sign of fatigue immediately before the screen broke.

The 1507 gm. of residue was cooled in an ice bath, thus effecting the separation of about 250 ml. of water. Upon removing the rest of the water by distillation, the main part of the residue was found to boil between 165° and 180° (u.c.), indicating a mixture of furfural and furfuryl alcohol. This residue could presumably be repassed through the catalyst until a near-theoretical conversion to sylvan was produced. Plans to accomplish this were interrupted by the breaking of the screen.

#### F. Hydrogenation of Sylvan to Tetrahydro-sylvan

In these experiments, a water bath replaced the Wood's metal bath around the vaporizing flask.

##### CATALYST NO. 1

Fifty grams of Raney nickel suspended in boiling water was activated by the slow addition of a solution containing 50 gm. of NaOH. After the reaction had ceased, the mixture was filtered on a Buchner funnel and washed with distilled



water. It was re-suspended in water and 100 gm. of activated charcoal lumps added. By again filtering, charcoal covered with nickel catalyst was left on the filter. This was placed in the catalyst chamber and dried at 200°.

At a furnace temperature of 125° and with the vaporizing flask at room temperature, 50 gm. of sylvan was passed through the catalyst. Hydrogen was used up fairly rapidly for a few minutes at a time; then flushing was necessary to restore the rate. This indicated the accumulation of a decomposition gas. The furnace temperature was lowered to 115°, where the reaction appeared to proceed more steadily. The hydrogenation rate was considerably lower at temperatures much below 115°. At one time, when the hydrogenation rate had dropped to a low value due to the supposed accumulation of a decomposition product, a sample of gas was withdrawn for analysis.

When all the sylvan had passed through, 26.3 gm. of product was found in the receivers. This loss of 23.7 gm. may be accounted for both by the decomposition of the compound as it passed over the catalyst and by the amount of vaporized product flushed out with the frequently renewed hydrogen.

Analysis of gas sample:

CO <sub>2</sub>	-	0.70%	CO	-	1.05%
Unsaturated HC's	-	0.70	H <sub>2</sub>	-	18.40
O <sub>2</sub>	-	0.25	Inert	-	0.74
Saturated HC's	-	77.20	(C <sub>1.05</sub> H <sub>4.06</sub> )		

This analysis indicates that the decomposition takes the form of the hydrogenolysis of a C-C bond, splitting off the CH<sub>3</sub> group to form methane. The high percentage of methane present with the resulting low concentration of H<sub>2</sub> readily accounts for the low rate of hydrogenation accompanying this accumulation of inert gas.

Distillation of products: An appreciable portion smelling like furan distilled at 30-32° but did not condense. This is in support of the assumption that hydrogenolysis of the bond between the furan nucleus and the methyl group occurred, forming methane and furan.

After a large portion had distilled between 55° and 77°, only 5 gm. was collected between 77° and 82°. This was the tetrahydro-sylvan fraction. A small amount of residue remained in the flask. Based on the 26.3 gm. of product collected, the yield of tetrahydro-sylvan fraction was 20%.

#### CATALYST NO. 2

The conclusion that Raney nickel in its usual form was too active for this hydrogenation led to the study of other forms of Raney nickel.

A catalyst was prepared by distributing 50 gm. of unactivated Raney nickel on 100 gm. of activated charcoal lumps. At furnace temperatures from 100° to 250°, sylvan was passed through this catalyst, but no hydrogenation occurred.

CATALYST NO. 3

Eighty grams of Raney nickel suspended in boiling water was treated with a solution containing 5 gm. of NaOH. This is 6.25% of the NaOH normally used. The catalyst was distributed on 150 gm. of activated charcoal as in the procedure for catalyst #1, placed in the hydrogenator and dried in a stream of hydrogen at 200°.

At furnace temperatures between 110° and 135°, 150 gm. of sylvan was passed through this catalyst in three batches. The temperature at which the hydrogenation proceeded most smoothly was 115-120°. Above this, frequent flushing was necessary. The hydrogenation rate was never very high.

On distilling the 131 gm. of product, 25-30 cc. came over between 70° and 78°. The tetrahydrosylvan fraction, boiling between 78° and 82°, weighed 64.5 gm. On the basis of amount of product, the yield was 47%.

The physical constants of the tetrahydrosylvan fraction received are compared below with the constants found in the literature.

	<u>Product</u>	<u>Tetrahydrosylvan</u>
B. Pt.	78-82°	78-80°
n	1.4065 <sup>21</sup>	1.40595 <sup>21</sup>
d	.8580 <sup>21</sup> <sub>21</sub>	.8534 <sup>21</sup> <sub>15</sub>

By repassing the 25-30 cc. of product boiling below 78° through the catalyst, a yield of well over 50% should be obtained.

Another catalyst prepared with the same amounts of materials gave the same results.

#### CATALYST NO. 4

One hundred grams of Raney nickel was suspended in boiling water and a solution containing 8 gm. of NaOH was slowly added. This Raney nickel, activated with 8% of the NaOH usually used, was distributed on charcoal as before and dried in the catalyst chamber.

At furnace temperatures between  $112^{\circ}$  and  $140^{\circ}$ , the hydrogenation rate was higher than with the previous catalysts. From 100 gm. of sylvan, the following products were obtained:

Total weight of product	-	79.0 gm.
Boiling below $75^{\circ}$	-	29.5 gm.
Boiling from $75-85^{\circ}$	-	36.0 gm.
Boiling above $85^{\circ}$	-	13.5 gm.

This is a yield of 43.5%. The accumulated fractions boiling above  $85^{\circ}$  were fractionated and found to include secondary amyl alcohol (b. pt.  $119^{\circ}$ ) and methyl propyl ketone (b. pt.  $102^{\circ}$ ). The alcohol was identified by its 3,5-dinitrobenzoate melting at  $60^{\circ}$ . The methyl propyl ketone was identified by the 2,4-dinitrophenyl hydrazone (m. pt.  $141^{\circ}$ ) and the semicarbazone (m. pt.  $108^{\circ}$ ).

Another catalyst was prepared in exactly the same manner as the previous one. The hydrogenation rate was quite low, and after repassing the unchanged portions several times,

the final yield was only 32.6%.

#### CATALYST NO. 5

Fifty grams of Raney nickel was activated with 3 gm. of NaOH (6% of the amount usually used) and distributed on charcoal as before.

One hundred grams of sylvan plus 31 gm. of the unchanged sylvan fraction from previous runs were the starting materials. The product, after repassing the unchanged portions several times, consisted of:

Boiling below 50°	-	2 gm.
Boiling from 50-75°	-	28.5 gm.
Boiling from 75-85°	-	46.0 gm.
Boiling above 85°	-	<u>21.0 gm.</u>
Total product	-	97.5 gm.

Based on the amount of product received, this is a 46% yield of tetrahydrosylvan. It is not yet understood why this and the preceding catalyst were less efficient than catalysts #3 and #4.

#### CATALYST NO. 6

A solution of nickel nitrate was precipitated by ammonium carbonate. The precipitate was washed, suspended on charcoal lumps, placed in the catalyst chamber and reduced to metallic nickel at 225° in a stream of hydrogen.

Fifty grams of sylvan was passed through this catalyst

at a furnace temperature of  $105^{\circ}$ . Although the hydrogenation rate was rather low, over 50% by volume of the product boiled between  $77^{\circ}$  and  $82^{\circ}$  and had the physical properties of tetrahydrosylvan. A noticeable amount of the product boiled between  $30^{\circ}$  and  $35^{\circ}$  and smelled like furan.

#### CATALYST NO. 7

A nickel catalyst was prepared by adding 30 gm. of KOH to a suspension of 100 gm. of charcoal lumps in a solution containing 80 gm. of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . After washing the product on a Buchner funnel, it was placed in the catalyst tube and reduced at  $230^{\circ}$ . Near the end of the reduction period, a strong odor of ammonia was noticed as in certain of the copper catalysts mentioned before.

Between furnace temperatures of  $110^{\circ}$  and  $150^{\circ}$ , no hydrogenation of sylvan was accomplished.

#### CATALYST NO. 8

A nickel acetate catalyst was prepared by soaking 100 gm. of activated charcoal lumps in a hot solution of nickel acetate. After partially drying, the process was repeated twice, leaving crystals of nickel acetate well-covering the charcoal. This was dried and decomposed in the hydrogenator. Decomposition was not evident until the furnace temperature was  $230^{\circ}$ . A maximum of  $300^{\circ}$  was used.

Fifty grams of sylvan was passed through this catalyst at furnace temperatures between  $115^{\circ}$  and  $155^{\circ}$ . The higher

temperature seemed to be better, although the hydrogenation rate was never very high.

Based on the 42 gm. of product received, the yield of tetrahydrosylvan was 15.9%.

#### CATALYST NO. 9

A copper chromite catalyst prepared in the same manner as catalyst 20 in Part D was tried with furnace temperatures between 90° and 250°. No hydrogenation of the sylvan passed through occurred.

#### CATALYST NO. 10

Six grams of a reduced nickel catalyst prepared according to the directions of Covert, Connor and Adkins (34) was placed in a Parr hydrogenation bomb with 32 gm. (1 mol) of sylvan. It was hydrogenated at an original pressure of 1480 lbs. and a temperature of 250° for two hours. It was necessary to refill the bomb twice. The yield of tetrahydrosylvan from this reaction was 68%.

### G. Dehydration of Tetrahydrosylvan

Since the patents covering the dehydration of tetrahydrofurans (6, 28) have included all of the common and some of the uncommon dehydration catalysts, the problem did not seem to be as much that of discovery as it was of verification. A conclusion that can be drawn from the following

cursory investigation, however, is that there is much yet to be discovered about the reaction before it is commercially feasible.

#### CATALYST NO. 1

Mercuric phosphate was precipitated on activated alumina from  $\text{HgCl}_2$ ,  $\text{Na}_3\text{PO}_4$  and  $\text{H}_3\text{PO}_4$ . After washing and drying, it was placed in the catalyst tube and dried at  $300^\circ$  in a stream of nitrogen.

Fifty grams of tetrahydrocyclopentadiene was placed in the vaporizing flask, kept at  $70^\circ$ , and the recirculation pump was started, with the furnace at  $325^\circ$ . Mercury was noticed to distill from the catalyst during the run.

Upon distillation of the product, 5 to 6 ml. of a fraction boiling between  $41^\circ$  and  $45^\circ$  was obtained. A fraction of approximately the same volume was received between  $26^\circ$  and  $41^\circ$ . Since most of this fraction boiled at the lower temperature, it was thought that this fraction was chiefly the 1,4-isomer of piperylene. The lower-boiling part of the fraction disappeared before the physical constants were measured.

The physical constants of the fraction boiling between  $41^\circ$  and  $45^\circ$ , as compared with those of piperylene, are as follows:

	<u>Product</u>	<u>Piperylene</u>
n	0.699 <sup>20</sup>	0.696
d	1.430 <sup>15</sup>	1.440 <sup>16</sup>



One milliliter of this fraction was polymerized to a rubbery mass with a few crystals of  $\text{AlCl}_3$ . The rest of the diene fraction was mixed with an ether solution of maleic anhydride in order to obtain the addition product melting at  $62^\circ$ . Instead, a thin white film of rubber was scraped from the bottom of the flask after four days.

#### CATALYST NO. 2

Four hundred cubic centimeters of activated alumina (14-30 mesh) was moistened with syrupy  $\text{H}_3\text{PO}_4$ . The catalyst tube was filled with this mixture and dried for 4 hours at  $310^\circ$  in a nitrogen stream.

At furnace temperatures between  $330^\circ$  and  $350^\circ$ , 50 gm. of tetrahydrofuran was passed through the catalyst. Distillation of the product gave the following fractions:

Boiling below $37^\circ$	-	5.5 cc.
Boiling from $37-50^\circ$	-	9.5 cc.
Boiling from $50-85^\circ$	-	18 gm.
Boiling above $85^\circ$	-	4 gm.

A total of 100 gm. of tetrahydrofuran and 41 gm. of the recovered fraction boiling between  $50^\circ$  and  $85^\circ$  was sent through the catalyst. The total amount of product boiling between  $37^\circ$  and  $50^\circ$  was 23 cc. About half this volume of lower-boiling products was formed.

The catalyst was found to have set to a hard mass impossible to remove from the catalyst tube.

### CATALYST NO. 3

Four hundred cubic centimeters of activated alumina lumps was suspended in a solution of 100 gm. of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{AlPO}_4$  was precipitated by the addition of a solution containing 35 gm. of ammonium acid phosphate. The mixture was washed and partially dried on a Buchner funnel, then placed in the catalyst tube and dried at  $350^\circ$ . Brown fumes of nitrogen oxides were given off from the catalyst as it was being dried and also as it was being used. Fifty-three and five-tenths grams of tetrahydrosylvan was passed over the catalyst. On distilling the product, the fraction boiling below  $37^\circ$  was larger than the piperylene fraction. The fraction boiling above  $85^\circ$  was also larger than usual.

### CATALYST NO. 4

A thick paste of kaolin and water was made and spread in a layer in the bottom of a large evaporating dish. This was heated with a Meker burner until dry, was broken into small lumps and placed in a catalyst tube 30 cm. in length and 3 cm. in diameter. After further drying at  $400^\circ$  in a nitrogen stream, 50 gm. of tetrahydrosylvan was passed through in a stream of nitrogen over a period of 2 hours. At the end of this time, the catalyst was quite black. No recirculation device or vaporizing flask was used, the tetrahydrosylvan being dripped into a warm portion of the catalyst tube.

The product weighed 44.9 gm., 7.6 cc. of which was water.

The following fractions were received upon distillation of the hydrocarbon layer:

Boiling below 37° - 5.0 gm.

Boiling from 37-47° - 6.1 gm.

Boiling from 48-75° - 10.0 gm.

Boiling from 75-85° - 5.8 gm.

Boiling above 85° - 5.8 gm.

Loss in distillation - 3.2 gm.

Based on the amount of water received, 72.7% of the starting material was dehydrated. The yield of piperylene fraction was, however, 17.4% (on the basis of the product recovered).

#### CATALYST NO. 5

A catalyst was prepared from kaolin in the same manner as for catalyst #4 and placed in the catalyst tube of the same apparatus and dried at 400° (the temperature used for the dehydration in this and the last experiment).

The second receiver, cooled in a dry ice-acetone receiver as before, was connected to an aspirator and, with a pressure of 60-85 mm., 50 gm. of tetrahydrofuran was dripped through in a stream of nitrogen over a period of 80 minutes. The catalyst at the end of this operation was grey--distinctly lighter than catalyst #4.

The product weighed 41.8 gm., 8.5 gm. of which was a water layer. Distillation of the hydrocarbon layer yielded

the following fractions:

Boiling below 37°	-	3.5 gm.
Boiling from 37-47°	-	10.1 gm.
Boiling from 48-85°	-	13.5 gm. (only a few drops above 75°)
Boiling above 85°	-	2.9 gm.
Loss in distillation	-	3.0 gm.

Based on the amount of water collected, 81.3% of the starting material was dehydrated. The yield of piperylene fraction, based on the product recovered, was 30.3%.

In comparing the last two catalysts, it is seen that operation under reduced pressure possesses the following advantages:

1. Reduces the amount of charring.
2. Raises the yield of piperylene.
3. Reduces the formation of higher-boiling compounds.
4. Reduces the amount of product boiling below piperylene.
5. No appreciable amount of product was lost by its not condensing at the low pressure used.

Polymerization of the piperylene fraction: Nine and a half grams of the piperylene fraction boiling closest to 43° was used for the polymerization. The quantities of the other materials were:

Carbon tetrachloride - 1.3 gm.

Acrylonitrile - 3.0 gm.

Aqueous solution - 25.0 cc.  
(H<sub>2</sub>O plus 2.5 gm. ammonium oleate  
plus .12 gm. NaBO<sub>3</sub>)

After adjusting the pH to between 7 and 9 with NaOH, the mixture was sealed in a thick tube. The tube was then shaken for 45 hours, while kept at temperatures between 70° and 80°. At the end of this time, the tube was opened. Part of the polymer had already coagulated and the solution, on testing, was slightly acid. Five cubic centimeters of 10% HOAc coagulated the rest. About 8 gm. of a rubbery mass was obtained. This was kneaded in water, then in dilute ammonia and then in water again to remove oleic acid.

Mixing the sample with 15% by weight of ZnO and vulcanizing with 3% S improved its rubber-like properties.

### III. SUMMARY OF RESULTS

1. Two forms and sizes of a suitable apparatus for vapor phase catalytic studies have been built and described.

A recirculation device is employed for the conservation of materials.

2. More than twenty catalysts for the vapor phase hydrogenation of furfural to sylvan were tried. The most suitable catalyst was copper chromite, from which near-theoretical yields can be obtained in only a few passages. The only suitable carrier, of those tried, was activated charcoal.

3. The activity of several catalysts for the hydrogenation of sylvan to tetrahydro-sylvan has been observed. The yields obtained ranged up to 69%, but a commercially applicable catalyst was not found. Investigations now in progress with partially activated Raney nickel catalysts in the liquid phase may reveal a suitable one (35).

Partially activated Raney nickel has been shown to be more efficacious than the completely activated form in the vapor phase hydrogenation of sylvan to tetrahydro-sylvan. It is possible that this type of Raney nickel may find more extended applications.

4. The dehydration of tetrahydro-sylvan to 1,3-pentadiene was accomplished in yields up to 30% with the four catalysts

studied. Dehydration at a greatly reduced pressure in the case of the kaolin catalyst almost doubled the yield, and it is presumed that this refinement may improve the yield of any of the dehydration catalysts.

5. Emulsion polymerization, a method not previously applied to piperylene, has been utilized in producing a satisfactory synthetic rubber sample.

6. This study has shown that furfural, a non-critical and abundant raw material, is potentially an economical source of synthetic rubber. The results of this investigation fully warrant a more complete study with the immediate objective of large-scale utilization of the process.

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