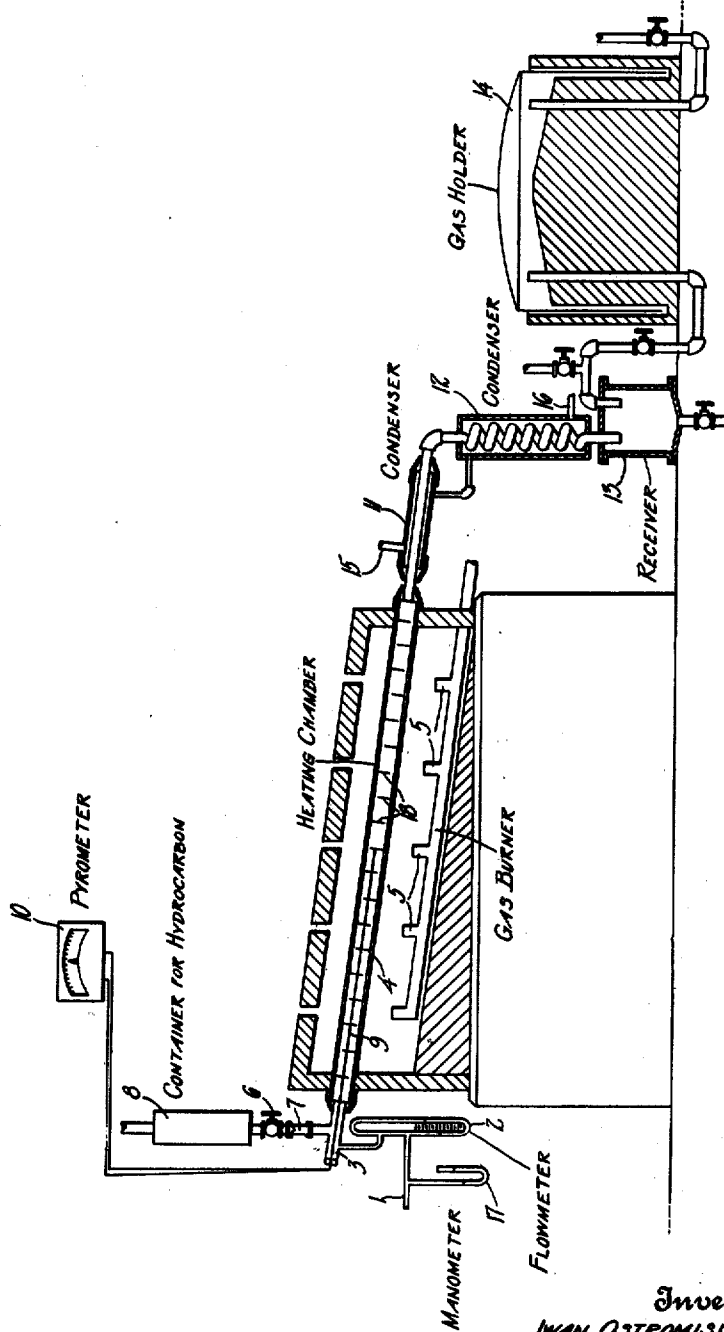


June 9, 1925.

1,541,175

I. OSTROMISLENSKY ET AL
PROCESS FOR PRODUCING STYROL AND ITS HOMOLOGUES
FROM AROMATIC HYDROCARBONS
Filed May 7, 1924



Inventors
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By their Attorney
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UNITED STATES PATENT OFFICE.

IWAN OSTROMISLENSKY AND MORRIS G. SHEPARD, OF NEW YORK, N. Y., ASSIGNORS
TO THE NAUGATUCK CHEMICAL COMPANY, OF NAUGATUCK, CONNECTICUT, A
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PROCESS FOR PRODUCING STYROL AND ITS HOMOLOGUES FROM AROMATIC HYDRO-
CARBONS.

Application filed May 7, 1924. Serial No. 711,583.

To all whom it may concern:

Be it known that we, IWAN OSTROMIS-
LENSKY and MORRIS G. SHEPARD, a citizen
of Russia and a citizen of the United States,
respectively, both residents of New York,
county and State of New York, have in-
vented certain new and useful Improve-
ments in Processes for Producing Styrol
and its Homologues from Aromatic Hydro-
carbons, of which the following is a full,
clear, and exact description.

This invention relates to the production
of styrol and its homologues from hydro-
carbons having eight or more carbon atoms,
such as ethyl benzol, xylol, homologues and
analogues thereof, by pyrogenic decompo-
sition.

The objects of the present invention are
to provide a process of the kind described
which shall produce a high yield of styrol,
and its homologues, which shall be econom-
ical and can be carried out in a practical
way with simple apparatus.

The invention accordingly consists of a
process for making styrol and/or its homo-
logues which comprises heating a hydro-
carbon having at least eight carbon atoms
and at least 10 hydrogen atoms to a tem-
perature of approximately 450° C. to ap-
proximately 700° C., and partially decom-
posing the hydrocarbon to form a com-
pound having the general formula Ar.CH:CH_2 ,
where Ar. is aryl.

This case is a continuation in part of our
application Serial No. 648,751, filed June
20, 1923.

In carrying out the invention the appa-
ratus shown diagrammatically in the figure
may be employed. It comprises a source
of carbon dioxide or other neutral gas led
in by a pipe 1 through a flowmeter 2 by
means of pipe 3 into the interior of an
iron pipe 4 which is heated in any desired
manner to the required temperature, as by
gas burners 5. Communicating also with
this tube 4 through a valve 6 and sight glass
7 is a container 8 for the hydrocarbon. The
temperature is determined by means of a
thermocouple 9 arranged in the present em-
bodiment to record through the indicator 10
the temperature of the gas in the interior of
the tube at the middle. Electric or other
heating means may be employed if desired.
The tube 4 leads into the Liebig condenser

11 and on into the worm condenser 12
which is in turn connected to the receiver
13. The liquid products are those con-
densed and collected in the receiver 13 while
the non-condensable gases pass on into the
gas holder 14. The condensers 11 and 12
are cooled by water led in at 15 and dis-
charged at 16. The manometer 17 acts
simultaneously as a pressure gauge and
safety device. The baffles 18 are used to
insure that the fluid is uniformly heated.

The processes for producing styrol, its
homologues and analogues may be divided
into two groups, which are designated as
follows: (1) dehydrogenation of ethylben-
zene or its homologues at high temperatures
(450–700° C.); and (2) splitting off hydro-
carbons from various homologues or ana-
logues of benzol which have more than two
atoms of carbon in a side chain at 500–
700° C.

1. Dehydrogenation of ethyl benzol
and/or its homologues at high temperatures
(450–700° C.).

The general formula for the reaction here
occurring is



where Ar. is aryl.

Under this group comes the treatment
of ethyl benzol, the procedure for treatment
of which is as follows: Ethyl benzol is run
from container 8 into the interior of iron
tube 4 at a measured rate. The apparatus
having been previously cleared of air by
passing a stream of carbon dioxide or other
neutral gas from the pipe 1 therethrough
and the iron tube having been heated up
to approximately 650° C. as shown by the
indicator 10, this temperature is maintained
throughout the run within plus or minus
15° C. The rate of flow of ethyl benzol is
maintained at approximately 15 to 20 gms./
min. and the rate of flow of carbon dioxide
as indicated by the flowmeter 2 at 50 to
60 c. c./min., the pressure in the heating
chamber 4 being approximately atmos-
pheric. The internal diameter of the tube
for these conditions of temperature and rate
of flow should be 2 in. and the total length
of the heated portion (that within the fur-
nace) is 54 in. The total internal volume
of the reacting portion of the tube is there-
fore 170 cu. in. in round numbers. The
process is continuous, it being only neces-

sary to interrupt for repairs, etc. The reaction which takes place upon passage of the ethyl benzol through the heated tube is as follows:



Other reactions may take place and do take place to produce gas, carbon and tarry products. The styrol and tarry products are collected together in the container 13 while the gases pass to the gas holder 14. A process for separating the styrol from the tarry products is set forth in our co-pending application Serial No. 711,584, filed May 7, 1924. This process comprises distilling the mixture with steam, separating the distillate from water and drying it. The dried product is placed in an autoclave and heated approximately for 16 hours at 180° C.—200° C. Polymerization of styrol to form metastyrol occurs. An accelerator of polymerization may be employed, if desired. With benzoyl peroxide as an accelerator polymerization may be accomplished in approximately 8–12 hrs. at 180° C. After polymerization the autoclave is opened and its contents subjected to a fractional distillation, the final residue remaining above 145° C. representing metastyrol. Under the conditions of pressure and temperature and using an iron tube as indicated, the amount of styrol produced from a thousand gms. of ethyl benzol is approximately 250 gms. This quantity of product represents an efficiency of approximately 32%.

The term "efficiency" as used, means the per cent of the theoretic yield of styrol calculated on the basis of the actual ethyl benzol consumed in the process. In carrying out the above process, 220 gms. of ethyl benzol was recovered per 1,000 gms. of ethyl benzol used, which means that 780 gms. of ethyl benzol were consumed. The efficiency therefore on a percentage basis is $250 \times 100 \div 780$ or 32%. This calculation neglects the slight difference in the molecular weight of ethyl benzol (106) and styrol (104).

Instead of ethyl benzol which has the formula $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ the isomer xylol which also has the formula $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ may be employed under substantially the same conditions as those indicated above for ethyl benzol. The reaction may be expressed as $\text{C}_6\text{H}_4(\text{CH}_3)_2 = \text{C}_6\text{H}_5\text{CH}:\text{CH}_2 + \text{H}_2$. The amount of styrol produced from 1000 grams of xylol is approximately 50 grams and the efficiency approximately 20%.

The conditions given in the preferred embodiment above, have been varied in order to determine among other things, the optimum temperature for various tube materials, the optimum rate of flow of ethyl benzol

and the value of the use of a neutral gas to promote the flow of ethyl benzol through the heating tube.

An iron tube, due to the ease with which such tubes may be procured, has been indicated in the preferred embodiment above but numerous tests on other tubes show that iron may be replaced if desired. For example, quartz or copper tubing may be used in which case results quite similar to those with the iron tube are obtained. An exception is that of nickel. When nickel gauze was placed in an iron tube the results were not as satisfactory, the tendency being to form large quantities of gas and carbon at the expense of the desired product, styrol. The optimum rate of flow established will vary with variation of other factors of the apparatus and process, for instance, variations in the shape of the heating chamber and the distribution of heat in this chamber would influence the rate of flow and variations of pressure within the chamber would also influence the rate of flow. There is apparently a relationship of the volume within the heating chamber, the rate of flow and the temperature. This relationship may be expressed mathematically by the following formula:

$$\frac{.064V/R + T}{633} = K$$

in which V is the volume of the heated portion of the tube in cubic centimeters, R the rate of flow of ethyl benzol into the tube in grams per minute; T the temperature of the interior of tube at the middle point in degrees centigrade; and K the parameter varying between the values .8 and 1.2, the optimum efficiency being secured when $K=1$. The optimum efficiency is about 36%. This equation holds for all practicable rates of flow and all practicable sizes of tubes.

In order to determine the effect of the carbon dioxide or other neutral gas employed, a run was made using the iron tube as in the preferred embodiment in which no neutral gas was employed and it was found that the results were quite similar to those obtained when the neutral gas was used. However, the operation of the apparatus is simplified by the use of this neutral gas as the regulation of the rate of flow of ethyl benzol is thereby facilitated.

If any unchanged ethyl benzol or xylol is collected, this material may again be run through the apparatus to produce styrol with an efficiency substantially the same as given by the original ethyl benzol or xylol.

Other gases such as nitrogen and steam may be used to replace carbon dioxide the gas promoting flow through the heating chamber. The process may be run con-

tinuously. It requires little attention and is relatively economical.

In addition to ethyl benzol and xylol mentioned above, various other materials have been similarly treated falling within the present group. The products obtained on the raw materials are as follows: (a) orthomethyl styrol from orthomethyl ethyl benzol, (b) para methyl styrol from para methyl ethyl benzol, (c) symmetrical dimethyl styrol from 1, 3, 5. dimethyl ethyl benzol, and (d) ethyl styrol from diethyl benzol.

The starting points for (a) and (b) may be obtained by ethylating toluol. Symmetrical dimethyl styrol may be obtained by similar ethylation of xylol. The following is a tabulation of results obtained in the dehydrogenation of the isomer xylol and homologues of ethyl benzol into those of styrol following a similar process to that set forth for dehydrogenation of ethyl benzol.

25	A Boiling temperature of original mixture (C).	140°	175-185°	145-190°	160-165°	180°
	B Nature of active hydrocarbon.	xylol.....	1,3,5 dimethyl ethyl benzol	Orthomethyl ethyl benzol	Paramethyl ethyl benzol	Diethyl benzol
30	C Amount in grams per minute.	15 gms.	0.82 gms.	0.51 gms.	0.52 gms.	18 gms.
	D Duration of process.	1 hr. 7 mins.	6h. 45m.	3h. 15m.	7 hrs.	47 mins.
	E Mixture subjected to pyrogenization in gms.	1000 gms.	250 gms.	109 gms.	217 gms.	849 gms.
35	F Temperature of furnace (C).	650°	640-650°	580-620°	640-650°	650°
	G Liquid products obtained.	944 gms.	225 gms.	97 gms.	199 gms.	800 gms.
40	H Dry Hydrocarbons distilled with steam.	833 gms.	178 gms.	85 gms.	170 gms.	684 gms.
	I Nature of product styrol obtained.	-----	Meta-methyl styrol.	Orthomethyl styrol.	Paramethyl styrol.	Ethyl styrol.
45	J Content of styrol or homologues in distillate (steam) by analysis	5.7%	31.7%	28.6%	35.7%	23.8%

Whether the process is carried out in iron or quartz tubes the results are substantially as given above. Actually the above results were gotten using an iron tube for xylol and

a quartz tube for the other substances. The quartz tube had the following dimensions: 1" diameter by 27" long. It has been found that the relationship of the volume in the heating chamber, the rate of flow and temperature exists in a similar way for products other than ethyl benzol which may be expressed mathematically by the formula given in connection with the process employing ethyl benzol.

Instead of using ethyl benzol or its homologues separately, mixtures of ethyl benzol and/or of its homologues may be passed through a heated tube and a solution containing styrol and its homologues or the homologues alone obtained. For this purpose the mixtures of ethyl benzol and its homologues may conveniently be obtained by ethylating mixtures containing benzol, toluol and xylol, as for example the fractions obtained from coal tar, gas tar, etc. boiling from 80 to 130° C.

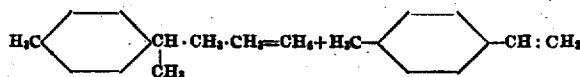
Ethyl benzol, xylol, etc. containing styrol in solution may also be used as raw material, for example, ethyl benzol which has already been subjected to the pyrogenization action of the hot tube. Such ethyl benzol or xylol, etc. containing styrol may be repassed through the tube. The result of such action is to enrich or increase the concentration of styrol.

For example, if a solution containing around 14% of styrol in ethyl benzol is passed through the hot tube under the usual conditions as set forth in our application Serial No. 648,751, filed June 30, 1923, the resulting raw product would contain around 30% styrol, whereas ordinarily using pure ethyl benzol the styrol content would run around 20%. The ethylbenzol recoverable from this raw product is essentially in the same proportion as that from pure ethyl benzol.

2. Splitting off hydrocarbons from various homologues or analogues of benzol which have more than two atoms of carbon in the side chain at 500-700° C.

The reaction involved in this group is as follows: $\text{Ar.C}_2\text{H}_4\text{R}=\text{RH}+\text{Ar.CH:CH}_2$, where Ar. is aryl and R represents an alkyl radical. This process has been investigated in connection with the treatment of cymene.

In carrying out the process with cymene the following reaction occurs:



Specifically the process employing cymene may be carried out as follows: Cymene is introduced from container 8 into the tube 4 of quartz at a rate of .5-.6 grams per minute. The tube is heated to 650° C., the diameter of the tube being 25 cm. and length subjected to heating 67 cm. A current of carbon di-

oxide at low pressure is passed from pipe 1 through the tube continuously during the whole process. The liquid reaction products condense in the receiver 13 which is water cooled. The methane formed in the reaction may be collected in the gasometer 14. The product resulting from treatment of cymene

in four hrs. and 20 minutes was 87 grams of liquid reaction products from 100 grams of cymene. By treating the liquid reaction product with steam 67 grams of crude methyl styrol appeared in the distillate and the remaining 20 grams of liquid products in the distilling flask. An analysis of the distillate showed that it contained 35.5 grams, i. e. 53.2% of paramethylstyrol, the main part of the by-products in this crude methy styrol being unchanged cymene which is easily regenerated under ordinary conditions. Eliminating the regenerated cymene, consequently the yield of methylstyrol under the conditions mentioned is 40-50% calculated on the weight of the original cymene taken.

Cymene may be obtained by transformation of a wide variety of terpenes. In particular it may be obtained from cheap varieties of turpentine which in turn are made by distilling shavings of pine-tree stumps with steam.

The processes described are simple and economical, and require simple apparatus only. They produce a relatively high yield of the desired product.

It will thus be seen that among others the objects of the invention above enumerated are achieved.

As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it will be understood that we do not intend to limit ourselves to the specific embodiment herein set forth except as indicated in the appended claims.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. A process for making compounds of the type ArCH:CH_2 where Ar represents aryl, which comprises heating a hydrocarbon having the general formula $\text{ArC}_2\text{H}_4\text{R}$ where R represents a monovalent substitution to a temperature of approximately $450^\circ\text{--}700^\circ\text{C}$. and partially decomposing the hydrocarbon to form ArCH:CH_2 .

2. A process for making compounds of the type ArCH:CH_2 where Ar represents aryl, which comprises heating a hydrocarbon having the general formula $\text{ArC}_2\text{H}_4\text{R}$ where Ar represents aryl and R represents a monovalent substitution, approximately to $450\text{--}700^\circ$, splitting off part of the side chain thereof to form ArCH:CH_2 .

3. A process for making compounds of the type ArCH:CH_2 where Ar represents aryl which comprises passing a stream of an aromatic hydrocarbon having the formula $\text{ArC}_2\text{H}_4\text{R}$ where R represents a monovalent substitution through a conduit heated to approximately $450^\circ\text{--}700^\circ$, collecting a mixture containing a substance having the formula ArCH:CH_2 , tarry matter and un-

changed $\text{ArC}_2\text{H}_4\text{R}$, and recovering the ArCH:CH_2 therefrom.

4. A process for making compounds of the type ArCH:CH_2 where Ar represents aryl which comprises passing a stream of an aromatic hydrocarbon having the formula $\text{ArC}_2\text{H}_4\text{R}$ where R represents an element through a conduit heated to approximately $450^\circ\text{--}700^\circ$, and decomposing the $\text{--C}_2\text{H}_4\text{R}$ portion thereof to yield ArCH:CH_2 .

5. A process for making compounds of the type ArCH:CH_2 where Ar represents aryl, which comprises heating a hydrocarbon having the general formula $\text{ArC}_2\text{H}_4\text{R}$ where Ar represents aryl and R represents hydrogen, approximately to $450\text{--}700^\circ\text{C}$., and splitting off hydrogen therefrom to form ArCH:CH_2 .

6. A process for making compounds of the type ArCH:CH_2 where Ar represents aryl, which comprises heating a hydrocarbon having at least eight carbon atoms and at least ten hydrogen atoms to a temperature of $450^\circ\text{C.}\text{--}700^\circ\text{C}$. approximately, and partially decomposing the hydrocarbon to form ArCH:CH_2 .

7. A process for making ArCH:CH_2 where Ar represents aryl which comprises passing a stream of a vaporized aromatic hydrocarbon having at least eight carbon atoms and at least ten hydrogen atoms through a conduit heated to a temperature of approximately 700° at a rate of flow of hydrocarbon and with a volume of conduit such that K falls within the limits of .8-1.2 in the formula

$$\frac{.064 V/R + T}{633} = K,$$

where V is the volume of the heated portion of the tube in cubic centimeters, R the rate of flow of material into the tube in grams per minute, T the temperature of the interior of the tube at the middle point in degrees centigrade, and K the parameter derived therefrom.

8. A process for making ArCH:CH_2 where Ar represents aryl which comprises heating a hydrocarbon having the general formula ArCH_2CH_3 to a temperature of approximately $450^\circ\text{C.}\text{--}700^\circ\text{C}$., and partially decomposing the hydrocarbon to form a compound having the general formula ArCH:CH_2 .

9. A process for making ArCH:CH_2 where Ar represents aryl which comprises passing a stream of an aromatic hydrocarbon having the formula ArCH_2CH_3 through a conduit heated to a temperature of approximately 450° to approximately 700°C . and splitting off hydrogen therefrom to form a compound having the formula ArCH:CH_2 .

10. A process for making ArCH:CH_2

where Ar represents aryl which comprises passing a stream of an aromatic hydrocarbon having the formula ArCH_2CH_3 through a conduit heated to a temperature of approximately 450°C . to approximately 700°C ., collecting a mixture containing a substance having the formula $\text{ArCH}:\text{CH}_2$, tarry matter and unchanged ArCH_2CH_3 , and recovering the substance $\text{ArCH}:\text{CH}_2$ therefrom.

11. A process for making styrol which comprises passing a stream of an aromatic hydrocarbon having the formula C_6H_{10} through a conduit heated to a temperature of approximately 450°C . to approximately 700°C . and liberating hydrogen from the aromatic hydrocarbon to form styrol.

12. A process for making styrol which comprises passing a stream of ethyl benzol through a conduit heated to a temperature of approximately 450°C . to approximately 700°C ., and splitting off hydrogen from the ethyl benzol to form styrol.

13. A process for making styrol which comprises passing a stream of vaporized ethyl benzol through a conduit heated to a temperature of approximately 700°C . at a rate of flow of hydrocarbon and with a volume of conduit such that K falls within the limits .8-1.2 in the formula

$$\frac{.064 V/R + T}{633} = K,$$

where V is the volume of the heated portion of the tube in cubic centimeters, R the rate of flow of material into the tube in grams per minute, T the temperature of the interior of the tube at the middle point in degrees centigrade, and K the parameter derived therefrom.

Signed at New York, New York, this 30 day of April, 1924.

IWAN OSTROMISLENSKY.
MORRIS G. SHEPARD.

where Ar represents aryl which comprises passing a stream of an aromatic hydrocarbon having the formula ArCH_2CH_3 through a conduit heated to a temperature of approximately 450°C . to approximately 700°C ., collecting a mixture containing a substance having the formula $\text{ArCH}:\text{CH}_2$, tarry matter and unchanged ArCH_2CH_3 , and recovering the substance $\text{ArCH}:\text{CH}_2$ therefrom.

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12. A process for making styrol which comprises passing a stream of ethyl benzol through a conduit heated to a temperature of approximately 450°C . to approximately 700°C ., and splitting off hydrogen from the ethyl benzol to form styrol.

13. A process for making styrol which comprises passing a stream of vaporized ethyl benzol through a conduit heated to a temperature of approximately 700°C . at a rate of flow of hydrocarbon and with a volume of conduit such that K falls within the limits .8-1.2 in the formula

$$\frac{.064 V/R + T}{633} = K,$$

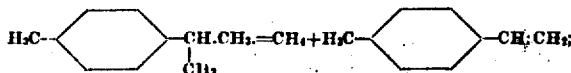
where V is the volume of the heated portion of the tube in cubic centimeters, R the rate of flow of material into the tube in grams per minute, T the temperature of the interior of the tube at the middle point in degrees centigrade, and K the parameter derived therefrom.

Signed at New York, New York, this 30 day of April, 1924.

IWAN OSTROMISLENSKY.
MORRIS G. SHEPARD.

Certificate of Correction.

It is hereby certified that in Letters Patent No. 1,541,175, granted June 9, 1925, upon the application of Iwan Ostromislensky and Morris G. Shepard, of New York, N. Y., for an improvement in "Processes for Producing Styrol and its Homologues from Aromatic Hydrocarbons," an error appears in the printed specification requiring correction as follows: Page 3, in the first column of the table, under the letter heading "I," strike out the word "styrol" and insert the same in the second column of the table opposite the same heading "I"; same page, line 108, strike out the formulæ and insert instead



and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

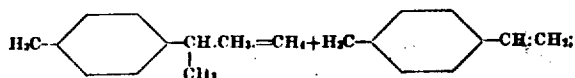
Signed and sealed this 22d day of June, A. D. 1926.

[SEAL.]

M. J. MOORE,
Acting Commissioner of Patents.

Certificate of Correction.

It is hereby certified that in Letters Patent No. 1,541,175, granted June 9, 1925, upon the application of Iwan Ostromislensky and Morris G. Shepard, of New York, N. Y., for an improvement in "Processes for Producing Styrol and its Homologues from Aromatic Hydrocarbons," an error appears in the printed specification requiring correction as follows: Page 3, in the first column of the table, under the letter heading "I," strike out the word "styrol" and insert the same in the second column of the table opposite the same heading "I"; same page, line 108, strike out the formulæ and insert instead



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Signed and sealed this 22d day of June, A. D. 1926.

[SEAL.]

M. J. MOORE,
Acting Commissioner of Patents.