

UNITED STATES PATENT OFFICE

2,492,985

OXIDATION OF HYDROCARBONS IN THE
PRESENCE OF LIQUID CATALYTIC FILMS

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This invention relates to oxidative reactions and particularly to the oxidation of hydrocarbons to form normally liquid oxygenated products, such as alcohols, esters, acids, ketones, aldehydes of the same or different number of carbon atoms than the parent hydrocarbon.

We have unexpectedly discovered, in accordance with our invention, that we can oxidize volatile hydrocarbons to oxygenated organic compounds of the types referred to above and can obtain superior yields of such oxygenated compounds with reduced amounts of undesirable products (i. e. the reaction results in very little burning or conversion of the hydrocarbon material to carbon oxides) or faster rates of reaction or both by contacting a gaseous mixture of at least one of such hydrocarbons and molecular oxygen in a reaction zone with a catalytic liquid in the form of a thin film, the hydrocarbon material being maintained substantially completely in the vapor phase and the amount of the catalytic liquid being minor in respect to the volume of the reaction zone.

We believe, although we do not wish to be bound in the practice of our invention by any theory thereof, that the superior results that we obtain in oxidations effected according to our invention are due to the use of a catalytic liquid film under conditions, as set forth herein, such that the catalytic film initiates a chain reaction which when propagates in the vapor phase with the formation of oxygenated products. We select the reaction conditions so that the reaction does not proceed with explosive violence with consequent formation of carbon oxides as the main products. We have found that the presence of inert gaseous diluents (such as nitrogen when air is used as the source of oxygen) and low densities or abnormally high densities of reactants slow down the rate of reaction many fold whereas the use of relatively high temperatures or insufficient cooling of the gaseous mixture causes the oxidation to proceed with undesirably rapid rates or even explosive violence with the consequent destruction of the desired products. We have further found that there is a minimum average distance between a hydrocarbon molecule in the vapor state and the catalytic liquid film below which the oxidation proceeds only slowly and that there is a critical range of density for any particular hydrocarbon in which superior results are obtained at a particular temperature.

It should be noted that an oxidation effected in accordance with our invention involves the

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following characteristics: (1) that it proceeds by a chain reaction; (2) that the chain reaction potentially may proceed at an undesirably high rate to give undesirable products; (3) that the reaction is capable of being catalyzed by catalysts which can be maintained as or within liquid films; (4) that it is possible to maintain the reacting materials substantially completely in the vapor phase under conditions which give practical reaction rates. Reactions of the oxidative type (which may include chlorination, nitration, and similar treatments of organic compounds such as hydrocarbons) frequently have these characteristics and our concept may be applied thereto. The manner in which our concept may be applied can be understood by the description herein of an exemplary operation applied to the oxidation of hydrocarbons by molecular oxygen.

As pointed out above, we obtain superior results when the reacting materials are substantially completely in the vapor phase and when we use a catalytic liquid in the form of a thin film, which is preferably flowing. Such a film and the manner of its use are essential features of our invention. We have found that, under the same conditions, virtually no reaction occurs in the absence of such a film and little, if any, reaction occurs with a film when the film contains no catalyst or the catalytic effect is neutralized by the presence of an oxidation inhibitor. The catalytic liquid forming the film may itself be a catalyst or it may comprise a carrier liquid containing a catalyst either in suspension or solution. A carrier liquid is preferably inert to oxidation or is similar or identical to one or more of the oxidation resistant products of the oxidation. Thus, for example, acetic, propionic, or butyric acids, carbon tetrachloride, benzene, phenylacetic acid, acetic anhydride, water and the like may be used as a carrier liquid for organic or inorganic salts or oxides of cerium, cobalt, copper, manganese, silver or uranium; or other liquids or catalysts such as those disclosed in Patent No. 2,265,948 issued to D. J. Loder on December 9, 1941, may be used. Furthermore, the liquid may contain, as disclosed in this patent, various initiators. Whether or not the catalytic film is a catalyst alone, such as cobalt stearate, or is a carrier liquid containing a catalyst in solution, such as glacial acetic containing cobalt acetate, or in suspension, such as colloidal osmium in water, it should be employed so as to present an extensive surface in the reaction zone and the amount of liquid present in the reaction zone at any given time should be minor in respect to the

volume of the reactant vapors present in the reaction zone.

The function of the catalytic liquid is to present a catalyzing surface to the gaseous reactants, and the thickness of the film formed by the liquid may therefore vary depending on its nature and manner of use, but, since superior results in regard to the rate and/or selectivity of the reaction are dependent on conducting the reaction substantially completely in the gaseous phase, it is preferred, as noted above, that the amount of the catalytic liquid present in the reaction zone should be minor in respect to the volume of gaseous reactants present in the reaction zone in order that the maximum amount of space be available for the chain reaction in gaseous phase. Under these conditions, we obtain a high reaction rate and gain the added advantage that the catalytic liquid dissolves a minimum amount for gaseous reactants (solution of considerable quantities of the gaseous reactants in the catalytic liquid tends to give undesirably low reaction rates). We have found that, when we control the depth of the liquid film so that the volume of the catalytic liquid is less than 10 volume per cent of the volume of the gaseous reactants, the effect is advantageous, and that particularly advantageous results are obtained when the volume of liquid is less than 5 volume per cent of the volume of the gaseous reactants, such as a preferred range of from about 0.01 to about 2 volume per cent.

In addition to the relative amount of the liquid, the relation of the extent of liquid surface to the volume of the gas phase is an important factor. When the liquid film flows over a surface which is also a heat exchange surface as, for example, the interior of a metallic vessel the exterior temperature of which is controlled as by heating or cooling, we have found that the distance between opposing film surfaces, which is a measure of the average distance of a molecule of reactant to the surface covered by the catalytic liquid film, should preferably be greater than about 0.3 to 0.4 millimeter. This distance should not be too great and is preferably less than 20 centimeters in the absence of some means of cooling the gas phase other than by heat exchange at the walls of the reaction zone. The distance between the opposing liquid films may be conveniently expressed as the ratio of the surface of the catalytic film to the volume of the gaseous reactants (i.e. the volume of the vapor phase). (The ratio referred to has the dimension of length⁻¹ and may be expressed as reciprocal centimeters or reciprocal feet). We have found, as a result of our investigations, that this ratio should be between about 0.2 to about 100 reciprocal centimeters and preferably between about 0.5 to about 20 reciprocal centimeters.

The effect of this ratio is one of the reasons for our belief that the reaction, when effected in accordance with our invention, is propagated as a chain reaction in the gaseous phase and is different from the usual liquid phase reaction in the catalytic liquid or a simple homogeneous gas phase reaction. If the reaction occurred principally at the interface between the catalytic film and the gaseous phase, the absolute value of the surface of the catalytic film should be more important than the ratio of the surface of the film to the volume of the gaseous phase. In order to ascertain the effect of surface, we filled a reaction zone with packing in the form of glass wool on which was maintained a film of cata-

lytic liquid consisting of cobalt acetate in acetic acid, and contacted this film with a mixture of butane and molecular oxygen under pressure. A similar run was made under identical conditions, except that the packing was absent, and the catalytic liquid was maintained as a flowing film on the walls of the vessel. The rate of oxygen absorption (in gram atoms per hour per liter of reaction volume) was about 1.7 times more rapid for the oxidation conducted in the unpacked zone (which had a ratio of surface area of the film to volume of the gaseous phase of about 1.15 reciprocal centimeters) than for the oxidation conducted in the packed zone (where the same ratio was about 116). Thus, in spite of a hundredfold increase in surface area, the reaction was slower. It should be noted, however, that the reaction space can be packed to advantage with loose packing, as, for example, Berl saddles or Raschig rings.

The film may be formed from the catalytic liquid by various methods, such as by flowing the liquid down the walls of a cylindrical vessel or over packing selected to give the proper surface-volume relations described herein, or by spraying a mist or droplets of the catalytic liquid into the reaction zone or by combinations of these and similar methods.

As stated above, we have found that it is important that the volume of the catalytic liquid occupy a minor portion of total reaction zone (or, in other words, that the ratio of the volume of the catalytic liquid to the volume of the gas phase be small). In our investigations, we found that, under otherwise identical conditions, an oxidation of butane in which the catalytic liquid occupies about 1 volume per cent of the reaction zone has a rate of oxygen absorption and a production of liquid oxygenated products more than 3 times greater than an oxidation conducted under identical conditions except that the catalytic liquid occupies about 25 volume per cent or more of the reaction zone. We also found that when the volume of the gaseous phase was maintained approximately constant but the volume of the catalytic liquid was increased eightfold (but was still minor in respect to the volume of the gaseous phase), the rate of oxygen absorption was approximately the same. Moreover, in all of the above oxidations performed in accordance with our invention, less than 5 per cent of the hydrocarbon material reacted was converted to carbon oxides (i.e. greater than 95% conversion to useful products). As can be understood from the above data, one of the factors in obtaining superior results in oxidations performed according to our invention is the maintenance of only a minor amount of the catalytic liquid in the reaction zone, relative to total volume of the reaction zone, an effective maximum being about 10 volume per cent, particularly advantageous results being obtained when amount of the catalytic liquid is less than 5 volume per cent, such as 0.02 to 2 volume per cent.

As stated above, it is advantageous to effect the oxidation under conditions that maintain the maximum amount of reactants in the gaseous phase. This effect is aided, as stated above, by maintaining a relatively minor amount of the catalytic liquid in the reaction zone. We also prefer to maintain temperature and pressure conditions such that the hydrocarbon is substantially completely in the vapor phase.

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Oxidative reactions may be effected, according to our invention, over a considerable range of pressures from substantially above atmospheric pressure, such as above about 5 atmospheres to relatively high superatmospheric pressures, such as about 300 atmospheres, the reaction rate being considerably reduced outside these values where the same amount of oxygen is used. A particularly effective range is between about 10 to about 100 atmospheres, and preferably between about 15 to about 75 atmospheres. Similarly a wide range of temperatures may be used, the reaction being generally conducted above a temperature at which oxidation is slow, such as about 100° C. and below a temperature of about 300° C. We prefer to use conditions of temperature and pressure that are correlated so that the hydrocarbon material in the reaction zone does not condense to form a liquid phase; such a condition is obtained by maintaining the hydrocarbon material above its dew point (the dew point of a condensable vapor being defined as that temperature and partial pressure at which reduction of temperature or increase of pressure causes the appearance of a liquid phase in a previously completely gaseous phase). Our invention, therefore, includes in its scope the oxidation of hydrocarbons whose boiling point at pressure substantially above atmospheric pressure, such as 5 atmospheres, is below the practical upper limit of temperature above which excessive formation of carbon oxides results. When the oxidation is effected under conditions such that 300° C. or above is the practical upper limit, suitable hydrocarbons will include volatile low molecular weight hydrocarbons that are substantially completely in the vapor phase at pressures of about 10 atmospheres or more at 300° C.

In accordance with a preferred embodiment of our invention, we oxidize at least one volatile low molecular weight hydrocarbon of the type described below at pressure substantially above the dew point of the hydrocarbon or hydrocarbons being oxidized by maintaining the reaction zone at a temperature above the dew point of said hydrocarbon or hydrocarbons and below about 210° C., such temperatures preferably being above about 125° C. In connection with this embodiment, we prefer to oxidize hydrocarbon material consisting essentially of at least one of the relatively volatile aliphatic hydrocarbons having from two to five carbon atoms inclusive, such as the paraffin hydrocarbons from ethane to pentane, inclusive, or the mono-olefins from ethylene or pentene. In general, we prefer to select, from among the broad ranges of conditions, those conditions which are suited to the reactivity of the particular hydrocarbon being oxidized and thus employ less severe conditions as the molecular weight, extent of molecular branching or extent of unsaturation increases.

We have found, as stated above, that the presence of inert diluents, such as nitrogen, decreases the rate of oxidation. As a means of increasing the rate of reaction we may use concentrated molecular oxygen, which may be obtained, for example, by the fractionation of liquid air. Such concentrated oxygen preferably contains less than 20 volume per cent of inert diluents, superior results being obtained when the oxygen contains less than 5 volume per cent, such as 2 per cent or less, of such diluents.

The concentration or partial pressure of hy-

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drocarbon material in the reaction zone is, according to our invention, maintained considerably in excess of the concentration of the molecular oxygen in the reaction zone, an effective ratio of the concentrations of hydrocarbon to oxygen being more than four to one, such as from about ten to one to fifty to one. Low relative concentrations of oxygen with high yields of liquid products may also be obtained by adding the oxygen in successive increments, the addition of these increments being spaced apart by time intervals such that the majority of the previous increment of oxygen has reacted before a following increment is introduced into the reaction zone.

In order to illustrate the present invention but not to be construed as a limitation thereof, the following examples are given:

Example I

A stainless steel bomb, adapted to be rocked through an angle of 60° at a rate of one cycle per second, was charged with 37.60 grams (649 millimoles) of n-butane (more than 99% pure), 1.7 milliliters (hereafter abbreviated as ml.) of glacial acetic acid and 1.0 ml. of glacial acetic acid containing 2 weight per cent of cobalt acetate. The 1.7 ml. of acetic acid charged was calculated to be the amount which would vaporize at 160° C. in the volume available (the volume of the bomb being about 210 ml.), thus insuring the maintainance of a liquid film. The 1.0 ml. of cobalt acetate in acetic acid was calculated to be the amount necessary to wet the interior surface of the bomb and provide a flowing thin film when the bomb was rocked as described above. The bomb and contents were heated to 160° C. and thereafter maintained at this temperature, the pressure in the bomb after heating being 575 pounds per square inch gauge (hereafter abbreviated as p. s. i. g.).

Concentrated molecular oxygen (over 99% pure) was added until the pressure was 625 p. s. i. g. After 5 minutes, 8.1 millimoles of oxygen were added after which the pressure was 655 p. s. i. g., whereupon a rapid reaction occurred as evidenced by a surge in pressure of about 30 p. s. i. g. followed by a rapid drop in pressure to about 615 p. s. i. g. The procedure outlined above was periodically repeated for 2 hours, with essentially the same results (i. e. a surge in pressure following the addition of oxygen followed by a rapid decrease in pressure and finally a leveling out at approximately a constant pressure), there being a total of 22 injections of oxygen varying from about 5 to about 25 millimoles of oxygen per injection amounting to a total of 263 millimoles.

The bomb was cooled and the contents removed and analyzed, the oxygenated derivatives being identified and determined by standard methods. A total of 31.06 grams of unreacted butane was recovered indicating that 17.4 per cent of the butane had reacted; the data also showed that 98.5 per cent of the oxygen had reacted. The liquid products, on a butane-free basis, amounted to 12.50 grams, exclusive of the acetic acid originally charged. In the following table, the total products are given in terms of the percentage of the total carbon content of the reacted butane necessary to yield the determined amount of the compound stated (e. g. 1 mole of CO₂ equals 25 per cent of 1 mole of re-

acted butane or 0.5 mole of butyl acetate equals 75 per cent of 1 mole of butane reacted).

Compound	Per Cent of N-butane reacted
Carbon dioxide and carbon monoxide.....	5.0
Acetaldehyde.....	1.3
Ethylacetate.....	3.3
Ethanol.....	7
Methyl ethyl ketone.....	18
Sec-Butanol.....	6
Sec-Butyl acetate.....	11
Acetic acid.....	18

In the above table, the amount of acetic acid initially present is not considered a product.

Example II

Using the same apparatus and procedure and the same amount of acetic acid and cobalt acetate as in Example I, 34.40 grams of isobutane were oxidized at 160° C. in 2 hours by repeated injections of oxygen totalling 202 millimoles. Analysis of the contents of the bomb indicated that 30.5 per cent of the isobutane had reacted as had 92.7 per cent of the oxygen and that the products, on the same basis stated above, were as follows:

Compound	Percent of Isobutane reacted
Carbon dioxide and carbon monoxide.....	2.0
Acetone.....	46
Methanol.....	15
tert.-Butanol.....	33
Acetic acid.....	2
Unidentified.....	2

Example III

Using the same apparatus and procedure and the same amount of acetic acid and cobalt acetate as in Example I, 37.71 grams of 2-butene (of more than 99 per cent purity) were oxidized at 160° C., using 169 millimoles of oxygen in one hour. Analysis of the contents of the bomb showed that 19.2 per cent of the butene-2 had reacted as had 92.4 per cent of the oxygen. The liquid products, on a butene-free basis, amounted to 14.00 grams, exclusive of the acetic acid originally charged. The products, on the basis stated above, were as follows:

	Per cent
Carbon dioxide and carbon monoxide.....	3.4
2,3-butylene glycol.....	39
Acetic acid.....	12
Acetaldehyde.....	12
Sec-butanol.....	10
Ethanol.....	8
Higher glycols and ethers (calculated as having the composition of butylene glycol)...	15

The 2,3-butylene glycol was found partially condensed as glycol acetates, acetaldehyde was found partially as acetals with ethanol and some of the acetic acid was condensed with ethanol as ethylacetate.

Example IV

Using the same apparatus and procedure and the same amount of acetic acid and cobalt acetate as in Example I, 33.93 grams of 1-butene (of 99 per cent purity) were oxidized at 160° C., using 160 millimoles of oxygen in two hours. Analysis of the contents of the bomb showed that 30.6 per cent of the 1-butene had reacted as had 91.7 per cent of the oxygen. The liquid products, on a

butene-free basis, amounted to 9.18 grams, exclusive of the acetic acid originally charged.

The data indicated that only 2.9 per cent of the hydrocarbon reacted had been converted to carbon dioxide and carbon monoxide. The liquid products were found to consist mainly of esters of 1,2-butylene glycol, together with some formic and propionic acid and some higher boiling compounds of butylene glycol.

Example V

Using the same apparatus and procedure and the same amount of acetic acid and cobalt acetate as in Example I, 36.58 grams of isobutene (of 99 per cent purity) were oxidized at 160° C., using 198 millimoles of oxygen in two hours. Analysis of the contents of the bomb indicated that 28.2 per cent of the hydrocarbon had reacted.

The data showed that 3.7 per cent of the hydrocarbon reacted had been converted to carbon dioxide and carbon monoxide. The liquid products, on an isobutene-free basis, amounted to 13.16 grams, exclusive of the acetic acid originally charged, and were composed principally of glycols, glycol esters, formic acid and acetone.

Example VI

In order to determine the effect of the vapor density of the hydrocarbon to the rate of reaction, a series of comparable runs in the same apparatus were made employing n-butane as the hydrocarbon and similar conditions as in Example I. The temperature, amount of catalyst and carrier liquid, amount and method of injection of oxygen were the same, but a variable vapor density (or pressure) of n-butane at the start of the run before the injection of any oxygen was employed in the different runs. The following results were obtained:

Vapor density of n-butane (in grams per ml.).....	0.002	0.09	0.13	0.18	0.33
Oxygen absorption in millimoles per hour per liter of reaction space.....	0	300	450	1300	500

The above data demonstrate that the rate of oxygen absorption is superior when the vapor density of the butane is between about 0.15 to about 0.25 gram per ml. (corresponding to a pressure range of about 550 to 700 pounds per square inch) when n-butane is oxidized at the temperature used (about 160° C.).

Additional data also showed that, in the same length of time, the amount of butane which had reacted was about twice as much when the vapor density was 0.18 gram per ml. as it was when the vapor density was 0.13 gram per ml., and about four times as much as when the vapor density was 0.33 gram per ml., further indicating the superiority of conducting the oxidation in the range of density (or pressure) stated.

These data confirm the view that the reaction may be slowed down by too great a density of the reactants, probably due to an extinction of the chain reaction at an early stage due to overcrowding of the molecules in the gaseous state.

Example VII

Using the same apparatus and procedure and the same amount of acetic acid and cobalt acetate as in Example I, 10.94 grams of isopentane were oxidized at 160° C. using 13 injections of oxygen over a period of six hours, the total amount of oxygen used being 186 millimoles. It was calculated that, at the stated conditions, the amount of isopentane used was insufficient to give a liquid phase. Analysis of the contents of the bomb indi-

cated that 52.6 per cent of the hydrocarbon had reacted.

The liquid product contained aldehydes, acids, ketones and other oxygenated compounds of incompletely determined nature, the principal portion of these compounds boiling below acetic acid.

Example VIII

Using the same apparatus and procedure and the same amount of acetic acid and cobalt acetate as in Example I, 28.3 grams of propylene (of more than 99 per cent purity) were oxidized at 180° C., using 23 injections of oxygen over a period of 88 minutes, the total amount of oxygen used being 306 millimoles. Analysis of the contents of the bomb indicated that 170 millimoles or 27 per cent of the propylene had reacted.

Analysis of the liquid products from this and another run made under almost identical conditions showed that a small amount of acetaldehyde had been formed, and that the liquid products boiling above 120° C. consisted principally of mixed formic and acetic esters of 1,2-propylene glycol. The material boiling above the esters mentioned consisted mainly of ester and ether condensation products of 1,2-propylene glycol. The fraction boiling below 120° C. contained free acetic and formic acids, as well as considerable amounts of isopropyl esters and acetals of formic and acetic acids with formaldehyde and acetaldehyde.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim as our invention:

1. In the oxidation of a volatile low molecular weight aliphatic hydrocarbon to form oxygenated organic compounds, the improvement which comprises reacting said hydrocarbon with molecular oxygen under conditions adapted to maintain said hydrocarbon substantially completely in the vapor phase at superatmospheric pressures of at least 5 atmospheres and in the presence of a catalytic liquid in the form of a thin film, the volume of said liquid being minor in respect to the volume occupied by the gaseous reactants.

2. The improvement of claim 1 in which the film is a flowing film.

3. In the oxidation of a volatile low molecular weight aliphatic hydrocarbon to form oxygenated organic compounds, the improvement which comprises reacting said hydrocarbon with concentrated molecular oxygen under conditions adapted to maintain said hydrocarbon substantially completely in the vapor phase at superatmospheric pressures of at least 5 atmospheres and in the presence of a catalytic liquid in the form of a thin film, the volume of said liquid being between about 0.01 to about 2 per cent of the volume occupied by the gaseous reactants.

4. The improvement of claim 3 in which the ratio of the surface of said film to the volume of

the vapor phase is between about 0.2 to about 100 reciprocal centimeters.

5. The improvement of claim 3 in which the ratio of the surface of said film to the volume of the vapor phase is between about 0.5 to about 20 reciprocal centimeters.

6. In the oxidation of a volatile low molecular weight aliphatic hydrocarbon to form oxygenated organic compounds, the improvement which comprises reacting said hydrocarbon with molecular oxygen in the presence of a catalytic liquid in the form of a thin film and at a temperature in the range of about 100° C. to about 300° C. and at a superatmospheric pressure of at least 5 atmospheres, said temperature and pressure being above the dew point of said hydrocarbon so as to maintain said hydrocarbon substantially completely in vapor phase, the volume of said catalytic liquid being minor in respect to the volume occupied by the gaseous reactants.

7. In the oxidation of a volatile low molecular weight aliphatic hydrocarbon to form oxygenated organic compounds, the improvement which comprises reacting said hydrocarbon with molecular oxygen in the presence of a catalytic liquid in the form of a thin film and at a temperature in the range of about 125° C. to about 210° C., and a superatmospheric pressure of at least 5 atmospheres, said temperature and pressure being above the dew point of said hydrocarbon so as to maintain said hydrocarbon substantially completely in vapor phase, the volume of said catalytic liquid being minor in respect to the volume occupied by the gaseous reactants.

8. The improvement of claim 7 in which the molecular oxygen contains less than 5 volume per cent of inert diluents.

9. The improvement of claim 7 in which the ratio of said hydrocarbon and molecular oxygen is less than 10 to 1.

10. The improvement of claim 7 in which the oxygen is periodically added in small increments.

11. In the oxidation of n-butane to form oxygenated organic compounds, the improvement which comprises reacting n-butane with concentrated molecular oxygen at a temperature of about 160° C. and at a partial pressure of n-butane in the reaction zone between 550 to 700 pounds per square inch and in the presence of a catalytic liquid in the form of a thin film, the volume of said liquid being between about 0.01 and about 2 per cent of the volume occupied by the gaseous reactants.

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The following references are of record in the file of this patent:

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Number	Name	Date
1,941,010	James	Dec. 26, 1933
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Certificate of Correction

Patent No. 2,492,985

January 3, 1950

ARISTID V. GROSSE ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 1, line 31, for the word "when" read *then*; column 3, line 20, for "amount for" read *amount of*;

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

Signed and sealed this 6th day of June, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.