

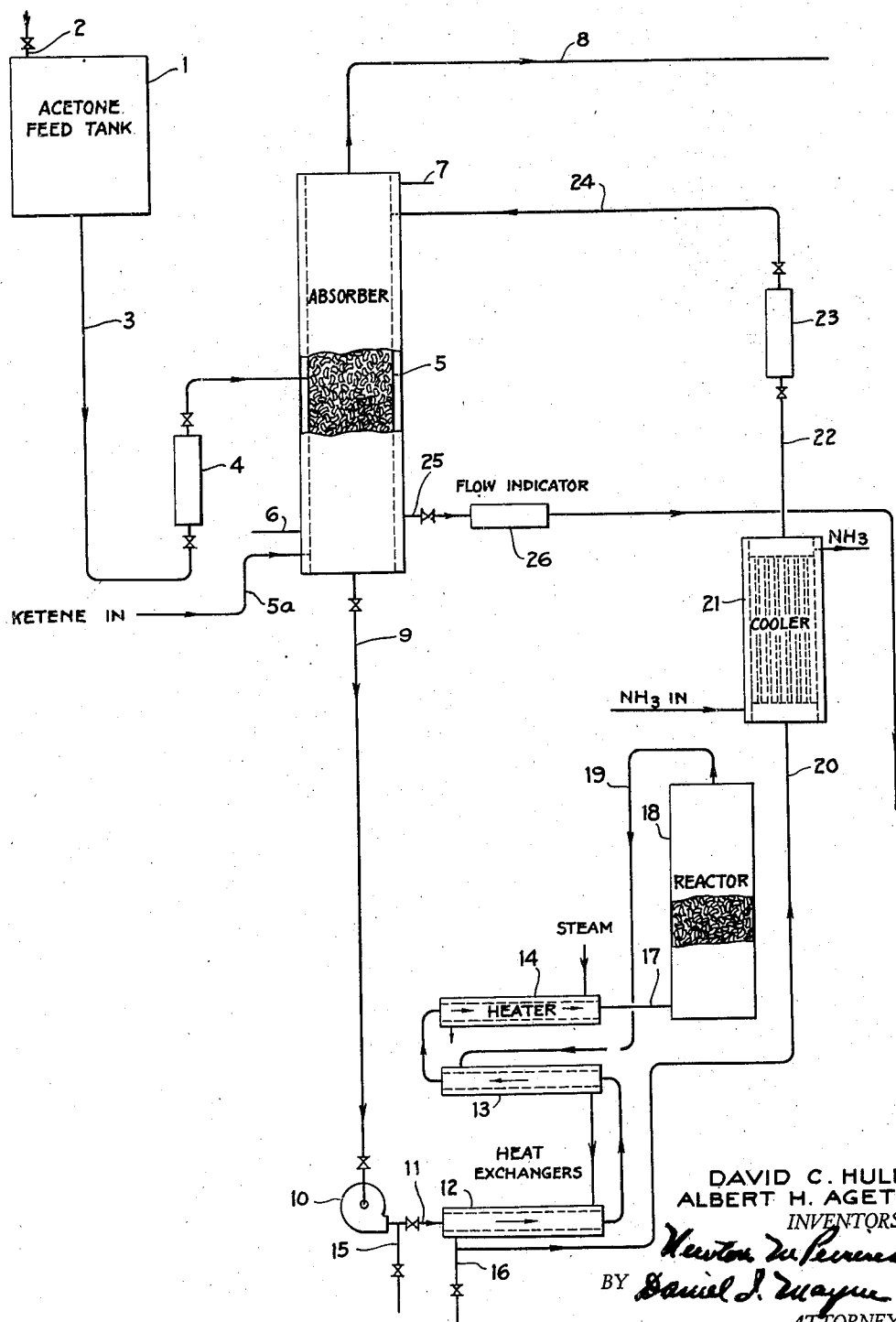
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D. C. HULL ET AL

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PROCESS FOR PRODUCING ENOL ACETATES

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PROCESS FOR PRODUCING ENOL ACETATES

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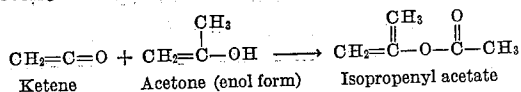
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This invention relates to a process for the production of enol acetates and more particularly to an improved continuous process for the production of isopropenyl acetate.

As is known from the work of Gwyn and Degering, U. S. Patent No. 2,383,965, enol acetates may be prepared by condensing ketene with a ketone in the presence of a mineral acid such as sulfuric, phosphoric or hydrochloric acid. The condensation is typified by the reaction between ketene and acetone as follows:



The methods disclosed in the patent are batch procedures in which ketene gas is passed through a batch or mixture of acetone containing the catalyst at elevated temperature and atmospheric pressure. For control of yields reliance is placed on variations of catalyst concentration, temperature and time of reaction as controlled by rate of addition of ketene.

It has been found, however, that batchwise operation carried out wholly at atmospheric pressure, especially at elevated temperatures, has many disadvantages, particularly the necessity for pumping large volumes of ketene, a notoriously reactive substance. In addition, batchwise procedures are uneconomical and wasteful, not only from the standpoint of the time factor involved in handling the reactants, but also from the standpoint of loss of reactants, particularly through the tendency of the ketene under such conditions to polymerize to diketene and to form quantities of tarry residues which contaminate the product and cut down the yield. Furthermore, in view of the fact that ketene is produced commercially under reduced pressure (see, for example, U. S. Patents Nos. 2,108,829 and 2,249,543) it is highly advantageous to provide a process of ketene utilization which can be readily tied in with commercial ketene production.

This invention has as an object to provide an improved process for the production of enol acetates. A further object is to provide a continuous cyclic process for the production of isopropenyl acetate and other enol acetates in which the loss of reactants and product are reduced to a minimum and other advantages obtained. Another object is to provide a substantially continuous method of ketene utilization which can be readily tied in with existing methods of ketene production. Other objects will appear hereinafter.

These objects are accomplished by the follow-

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ing invention, which in its broader aspects, comprises first absorbing ketene in one or more components, as in the desired ketone, such as acetone, at reduced pressure and low temperature, and then causing the ketene to react with the ketone or other carbonyl compound at elevated temperature and at atmospheric pressure. Specifically our invention involves absorbing ketene in acetone containing a condensation catalyst, such as sulfuric acid, at a pressure preferably below 150 mm. and at a temperature within the range of -50° C. to -10° C., preferably at -10° C., and thereafter causing the ketene to react with the acetone, for example, at or above atmospheric pressure and at a temperature within the range of 30-100° C., preferably at 65-70° C.

By the term condensation catalyst as used herein and in the claims we refer to those catalysts which are capable of catalyzing the condensation of ketene with a carbonyl compound such as acetone. Among such catalysts may be mentioned mineral acids such as sulfuric, phosphoric and hydrochloric acids, as well as organic acids such as p-toluene sulfonic acid, benzene sulfonic acid, m-benzene disulfonic acid, p-xylene sulfonic acid, p-nitro benzene sulfonic acid, m-nitro-benzene sulfonic acid and many other acid catalysts. While we may use any acid capable of giving a sufficiently strong acid reaction to promote enolization of the ketone and addition of ketene thereto, we prefer to employ sulfuric acid, particularly for the preparation of isopropenyl acetate.

In the following description and examples, we have set forth several of the preferred embodiments of our invention, but they are included merely for purposes of illustration and not as a limitation thereof.

The single figure of the drawing is a diagrammatic illustration in the nature of a flow sheet of one way in which our invention may be carried out in practice.

Referring to the drawing, numeral 1 designates a supply tank for the absorbent component, such as acetone, the material being introduced via valved conduit 2 and conveyed therefrom through conduit 3 and rotameter 4, to a steel jacketed absorber 5 which may have a diameter of 6 inches and a length of 20 feet, and provided with an appropriate means (not shown) for maintaining the interior thereof under reduced pressure and also with inlet conduit 5a for introduction of ketene gas at the prevailing pressure. Absorber 5 may be packed, as shown, with berl saddles. The contents thereof is cooled by circulating an ap-

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propriate cooling medium such as brine, or glycol through the jacket, the medium being introduced via inlet 5 and leaving through outlet 7.

The absorber is also supplied at the top with a conduit 8 for the escape of off gases and at the bottom with valved conduit 9 through which the liquid contents of 5 is conveyed to circulating pump 10, thence through valved conduit 11 to heat exchangers 12 and 13, which may be in the form of 14-gauge stainless steel tubes 20 feet long and of 3/4-inch outside diameter surrounded by stainless steel jackets of the same length and 1 1/4 inches in diameter and then, as shown, through heater 14, which may be in the form of a 20-foot section of stainless steel pipe of 1-inch outside diameter surrounded by a steel jacket of the same length and of 1 1/4 inches diameter and supplied with steam as the heat exchange fluid. Other points of access to the system are provided by way of valved lines 15 and 16, for example, for tapping off fluid from conduits 11 and 20 at the indicated points, if desired, or for adding materials.

Heater 14 is connected through conduit 17 with reactor 18 which may take the form of a cylindrical copper shell 12 inches in diameter and 36 inches long packed, as shown, with berl saddles. Both heat exchangers 12 and 13 and reactor 14 are placed at a level sufficiently below the level of absorber 5 to maintain the heat exchangers and reactor at at least atmospheric pressure by the hydrostatic head of the liquid in the circulating system or by this means and a pump.

The fluid contents of the reactor pass out at the top through conduit 19 and thence back into and through heat exchangers 13 and 12 counter-current to the flow of liquid passing in the inside thereof, in the direction indicated by the arrows. Upon emerging from heat exchanger 12 the fluid passes upwardly through conduit 20, thence through tubular cooler 21 which may consist of ten stainless steel tubes 3/4 inch in diameter and 20 feet long encased in a 6-inch standard gauge steel pipe jacket, emerging at the top thereof and passing through valved conduit 22, rotameter 23 and conduit 24 back into absorber 5 at the upper portion thereof.

Valved draw-off conduit 25 is provided for tapping off solution from the lower part of absorber 5, the flow of fluid therethrough being indicated by flow indicator 26.

Our process will be more readily understood by reference to a typical example thereof illustrating one way in which the invention may be carried out.

Example

Tank 1 is supplied with acetone at the rate of 91.7 lbs. per hour and sulfuric acid is added thereto at the rate of 1.3 lbs. per hour to maintain in the acetone a concentration of sulfuric acid of 1.4% by weight. The acetone solution is fed continuously through conduit 3 and rotameter 4 into absorber 5, passing downwardly there-through by gravity. The interior of the absorber is maintained under a reduced pressure of 45 to 50 mm. of mercury, while the absorber jacket is supplied with a cooling fluid maintained at a sufficiently low temperature to keep the contents of the absorber at a temperature in the vicinity of -10° C. Ketene gas at a pressure of 45 to 50 mm. is continuously introduced into the absorber through conduit 5a at the rate of 35.9 lbs. per hour and mingles with and is absorbed by the liquid acetone, the mixture (acetone, dissolved or

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absorbed ketene and catalyst) passing into conduit 9, thence to the circulating pump 10. Pump 10 is started and the mixture is pumped at the rate of five gallons per minute, first, through the heat exchangers 12 and 13 and finally through heater 14 where its temperature is raised to the reaction temperature of approximately 65-70° C.

The liquid then passes into reactor 18 which is also maintained at 65-70° C. and a pressure of 760 mm. In the reactor the ketene condenses with the acetone, in the presence of the sulfuric acid catalyst, to form isopropenyl acetate. The rate of flow of the mixture or recycling rate is so regulated as to permit a proper reaction time in the reactor. The crude mixture, which contains isopropenyl acetate, acetone, sulfuric acid and small amounts of acetic anhydride and diketene, then passes out of the reactor at the top thereof, thence via conduit 19, back through heat exchangers 13 and 12, and to cooler 21 where the temperature is again lowered to that prevailing in absorber 5. Finally the mixture passes to absorber 5 through conduit 24 and is recycled through the system.

As the acetone, catalyst and ketene are constantly being added to the system, the mixture containing the reaction product is constantly tapped out from the bottom of the absorber through conduit 25 in an amount corresponding approximately to the amount of the reactants and catalysts introduced. In a typical run carried out as just described, 91.7 lbs. of acetone, 1.3 lbs. of sulfuric acid and 35.9 lbs. of ketene per hour were introduced and recycled as indicated. Once the reaction was established there was tapped off from the absorber through conduit 25 at the rate of 125 lbs. per hour, a mixture composed of 67.3 lbs. acetone, 37.0 lbs. of isopropenyl acetate, 18.5 lbs. of high boilers and 1.3 lbs. of sulfuric acid, while 4.3 lbs. of off gases per hour were removed from the system via conduit 8, the gases containing 3.6 lbs. of non-condensables, 0.4 lb. of acetone and 0.3 lb. of ketene. The yield of isopropenyl acetate was approximately 90%.

While we have found it convenient to illustrate our process by reference to specific conditions and to specific procedural steps, it will be evident that many modifications of the process are possible within the scope of our invention. For example, carbonyl compounds other than acetone may be employed, the compound selected depending on the particular enol acetate it is desired to produce. Likewise, as indicated above, while we prefer to employ sulfuric acid as the catalyst, any acid capable of giving a sufficiently strong acid reaction to promote enolization of the ketone and condensation of ketene therewith may be used. Such details are shown in the prior art, as, for example, note U. S. Patent No. 2,383,965 already referred to, hence extended description herein is unnecessary.

The ketene used in our process may be produced in any convenient manner, as, for example, by the pyrolysis of any ketenizable substance such as acetone or acetic acid. In one of the more commonly employed commercial procedures, as already described, ketene is produced at a reduced pressure in the vicinity of 50 mm. of mercury by pyrolysis of acetic acid and this procedure may be conveniently used as the source of ketene in our process.

As indicated, our process comprises two major steps, (1) absorption of ketene in acetone (or other absorbent component such as another ketone, isopropenyl acetate or mixtures) at reduced pressure and low temperature, and (2) conden-

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sation of the ketene and a ketone at a higher temperature and at atmospheric pressure or above. In general, the pressure during the absorption step may be any low pressure below 150 mm., the preferred range being about 45-50 mm. While we prefer to carry out the absorption at a temperature in the vicinity of -10°C . it may be carried out at a temperature of -50°C . to -0°C . The concentration of the catalyst in the acetone is not especially critical and may be as usually used in the art (see U. S. Patent No. 2,383,965, aforementioned). Sulfuric acid and other acids in general may range from .001% to 5% by weight of the total weight of acetone and catalyst, the preferred value for the example described being about 1.4%.

Our invention has many advantages over the procedures heretofore employed for the production of isopropenyl acetate and similar enol acetates. For example, by operating under the conditions described above wherein the ketene is absorbed in the ketone at reduced pressure and at low temperature, we are able to increase the yields of isopropenyl acetate 10% or more above those obtained by carrying out the reaction entirely at atmospheric pressure and relatively elevated temperature. This is particularly true in the case where it is desired to employ a low pressure source of ketene, since under such circumstances it would be necessary, if operating under previously known procedures, to pump large quantities of ketene which is a notoriously reactive substance.

The necessity of handling ketene through a vacuum pump also has other disadvantages which are overcome by absorption of the ketene in a ketone and/or isopropenyl acetate or other component at reduced pressure, followed by withdrawing the ketene in solution through conventional equipment and then reacting at proper reaction temperatures which cannot be employed under reduced pressure, because of the low boiling point of the reacting materials. Furthermore, when ketene is held for any length of time, particularly at elevated temperature, many side reactions take place causing a loss in yield because of the formation of tarry residues and quantities of diketene. By previous absorption at reduced pressure in accordance with our invention, ketene is at no time at an elevated temperature in the pure state, and, therefore, does not have the opportunity of forming such by-products at any point along the temperature range from the preferred absorption temperature of -10°C . to the optimum reaction temperature of about 68°C .- 70°C .

From the preceding description it will be seen that the ketene is absorbed in acetone or other carbonyl compound to be reacted therewith. However, as the process progresses the enol acetate formed and circulated in a cooled condition to absorber 5 may likewise act as an absorbent for ketene. For example, in the instance of isopropenyl acetate which builds up in absorber 5, the boiling point of the absorbent becomes higher. In other words, the temperature of absorption may vary depending on whether the absorbent is substantially all carbonyl compound or substantially all enol acetate or intermediate for mixtures of the carbonyl compound and enol acetate. In the instance of the specific example herein concerning acetone and isopropenyl acetate, if the absorbent is comprised principally of acetone then the preferred temperature limit is the boiling point of the acetone under the reduced pressure conditions then prevailing. Likewise, if the

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absorbent is principally isopropenyl acetate (lean in acetone), then the temperature of absorption may be higher and will be the boiling point of the isopropenyl acetate under the reduced pressure conditions prevailing. Hence, the temperature of absorption may be varied over a substantial range, but will preferably be within the range of 0°C . to 50°C . discussed above.

While we have shown the incorporation of a carbonyl compound in absorber 5, enol acetate may be the absorbent and the carbonyl compound may, for example, be introduced through conduit 15, namely, just before the temperature is raised to cause reaction.

In general, therefore, in certain broader aspects of our invention our process comprises absorbing the ketene component in another component of the reaction, under a reduced pressure and temperature and thereafter causing the reaction to take place at a higher temperature and pressure as fully described herein. Many other advantages and changes will be apparent to those skilled in the art.

What we claim and desire to secure by Letters Patent of the United States is:

1. The process of preparing enol acetates which comprises absorbing ketene in a ketone having at least two hydrogen atoms on each carbon atom attached to the carbonyl group, in the presence of an acid condensation catalyst capable of enolizing the ketone and selected from the group consisting of sulfuric, phosphoric, hydrochloric, p-toluene sulfonic, benzene sulfonic, m-benzene disulfonic, p-xylene sulfonic, p-nitro benzene sulfonic and m-nitro-benzene sulfonic acids, at a pressure of not over about 150 mm. and a temperature within the range of -50°C . to 0°C ., and thereafter causing the ketene to react with the ketone to form an enol acetate at at least atmospheric pressure and at a temperature of 30 to 100°C .

2. The process of preparing isopropenyl acetate which comprises absorbing ketene in acetone containing an acid condensation catalyst capable of enolizing acetone and selected from the group consisting of sulfuric, phosphoric, hydrochloric, p-toluene sulfonic, benzene sulfonic, m-benzene disulfonic, p-xylene sulfonic, p-nitro benzene sulfonic and m-nitro-benzene sulfonic acids, at a pressure of not over about 50 mm. and a temperature of about -10°C ., and thereafter causing the ketene to react with the acetone at atmospheric pressure and a temperature of about 65 to 70°C .

3. The continuous process of preparing enol acetates by condensing ketene with a ketone in the presence of an acid condensation catalyst capable of enolizing the ketone and selected from the group consisting of sulfuric, phosphoric, hydrochloric, p-toluene sulfonic, benzene sulfonic, m-benzene disulfonic, p-xylene sulfonic, p-nitro benzene sulfonic and m-nitro-benzene sulfonic acids, which comprises maintaining a body of a solution of ketene, acetone, enol acetate and catalyst, controlling the temperature of the body of solution, continuously withdrawing a portion of the solution from said body, continuously adding ketene, acetone and condensation catalyst to the withdrawn portion, returning the part of the solution to which the ketene, acetone and catalyst were added to the body of the solution, and continuously removing from the recycling solution a portion thereof corresponding in amount to the amount of reactants and the catalyst introduced.

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5. The process of reacting a ketene with a ketone having at least two hydrogen atoms on each carbon atom attached to the carbonyl group in the presence of an acid condensation catalyst capable of enolizing the ketone and selected from the group consisting of sulfuric, phosphoric, hydrochloric, p-toluene sulfonic, benzene sulfonic, m-benzene disulfonic, p-xylene sulfonic, p-nitro benzene sulfonic and m-nitro-benzene sulfonic acids to form an enol acetate, which comprises absorbing ketene and at least one of the reaction components at a pressure below 150 mm. and at a temperature between -50°C . and 0°C ., causing the aforesaid components to flow together and during the flow raising the temperature and pressure sufficiently to cause a substantial amount of reaction between the ketene and the ketone.

6. The process of preparing isopropenyl acetate which comprises absorbing ketene in a liquid comprising acetone and containing an acid condensation catalyst capable of enolizing the acetone and selected from the group consisting of sulfuric, phosphoric, hydrochloric, p-toluene sulfonic, benzene sulfonic, m-benzene disulfonic, p-xylene sulfonic, p-nitro benzene sulfonic and m-nitro-benzene sulfonic acids, at a pressure not greater than 50 mm. and at a temperature between -50°C . and 0°C ., and thereafter causing the ketene to react with the acetone at a considerably higher temperature and pressure and obtaining at least a substantial part of said higher pressure by positioning said liquid at a higher level as respects the portion of the liquid undergoing reaction, whereby a substantial increase in pressure is obtained from the hydrostatic head of said liquid.

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7. The process of preparing enol acetates which comprises absorbing ketene in a ketone having at least one hydrogen atom on each carbon atom attached to the carbonyl group, in the presence of an acid condensation catalyst capable of enolizing the ketone and selected from the group consisting of sulfuric, phosphoric, hydrochloric, p-toluene sulfonic, benzene sulfonic, m-benzene disulfonic, p-xylene sulfonic, p-nitro benzene sulfonic and m-nitro-benzene sulfonic acids, at a pressure of not over 150 mm. and a temperature within the range of -50° to 0°C ., and thereafter causing the ketene to react with the ketone to form an enol acetate at at least atmospheric pressure and at a temperature of 30 to 100°C .

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

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OTHER REFERENCES

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Certificate of Correction

Patent No. 2,481,669

September 13, 1949

DAVID C. HULL ET AL.

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

Column 5, line 55, for "68°-70° C." read 65°-70° C.; column 7, before "5. The process" in line 1, insert the following claim—

4. *The continuous process of preparing isopropenyl acetate by condensing ketene with acetone, which comprises continuously feeding an acetone solution of sulfuric acid to a circulating stream composed of acetone, ketene, catalyst, and isopropenyl acetate, continuously introducing ketene into the stream, causing the ketene to be absorbed in the acetone at a pressure of not over about 50 mm. and at a temperature of about -10° C., thereafter raising the pressure of the mixture to atmospheric pressure and heating the solution to a temperature of about 65°-70° C., to cause the ketene to react with the acetone to form isopropenyl acetate, returning the mixture to the point of introduction of the reactants and continuously tapping off from the circulating stream a mixture containing acetone and isopropenyl acetate and catalyst.*

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 24th day of January, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.