

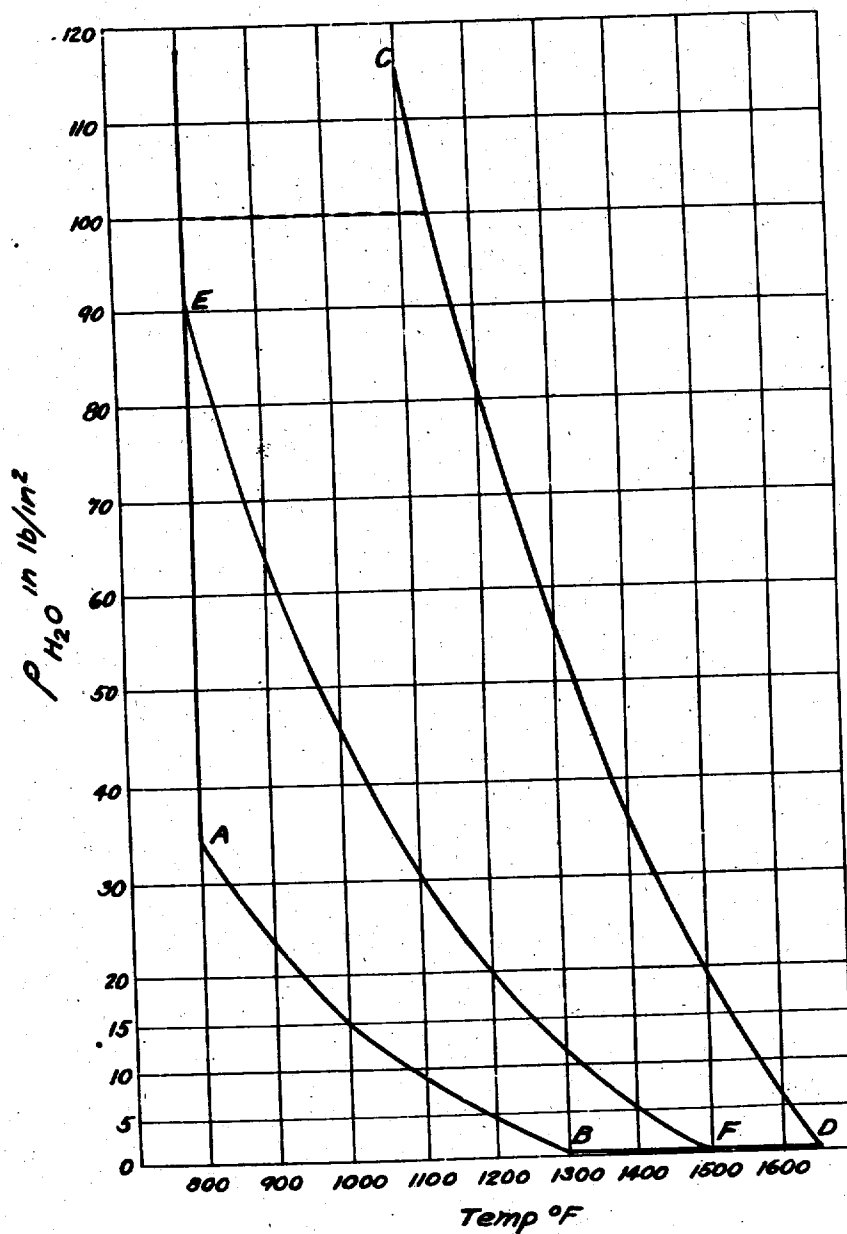
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J. R. BATES

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REGULATION OF CATALYTIC ACTIVITY

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REGULATION OF CATALYTIC ACTIVITY

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Continuation of application Serial No. 289,915,
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8 Claims. (Cl. 196—52)

The present invention relates to processes for preconditioning of active cracking catalyst for the cracking of selected types of charging stocks.

In the catalytic cracking of hydrocarbon materials for the production of gasoline it is well-known that many other materials besides gasoline are produced. Thus, the material leaving the catalyst during on-stream reactions includes hydrogen, hydrocarbon gases, and hydrocarbons heavier than gasoline, in addition to gasoline. However, not all of the materials produced leave the catalyst during on-stream reactions. Some of the heavy material is deposited within the catalyst as a coke-like material. This deposit in known processes of catalytic cracking is removed from the catalyst by burning. This coke represents a net loss since hydrocarbons are used up in its production. Also the greater the coke deposit the longer the regeneration period would have to be in proportion to the on-stream period in order not to exceed detrimental temperature levels during regeneration.

In the operation of catalytic cracking plants, prior to the present invention, the general practice has been to place an active cracking catalyst in the plant and to operate with that catalyst over a period of generally some weeks in an economically disadvantageous manner. The catalyst during this period undergoes changes and eventually comes to a condition in which the plant may be operated under economically desirable conditions. Whenever the catalyst has been renewed it has been necessary to repeat the same breaking in operation. During this breaking in period, the capacity of the plant is substantially reduced due to the necessity of decreasing the amount of oil fed to the catalyst and of introducing excessive amounts of steam for the purpose of limiting the amount of coke to an amount which can be removed by regeneration without harming the catalyst or the equipment. With any particular active cracking catalyst, it has not been known how to overcome the disadvantage of the high coke formation by such catalysts except by the above described control of cracking during the first several weeks of production.

It is accordingly an object of the present invention to precondition active cracking catalysts prior to use, whereby when a plant goes on stream, it is unnecessary to run uneconomically initially. It is a further object hereof to modify the activity in the preconditioning step, whereby

the activity, without being substantially killed, is shifted with resultant change in the relative proportion of products.

In accordance with the present invention the catalyst employed is a natural or synthetic silicious cracking catalyst. Such catalysts contain one or more metal oxides, which in general are selected from the group, alumina, zirconia, and beryllia. The catalyst is treated with steam at an elevated temperature under treating conditions sufficiently severe that the gasoline to coke ratio is increased at least 25% and sufficiently mild that the volume percent gasoline is not reduced more than 20% in the cracking of a stock of the type to be employed. The catalyst is then employed, after such pre-treatment, for the cracking of a stock of the type for which it was conditioned.

Active silicious cracking catalysts of the type to which the present invention relates may be either natural or synthetic. The natural catalysts are best illustrated by the activated clays such as are known in the art and disclosed in U. S. Patent No. 2,078,945 granted May 4, 1937, to Eugene J. Houdry. In clays the metal oxide present is alumina. Active synthetic catalysts, to which the present invention applies, are dried gels, containing silica and one or more metal oxides. While the commonly employed metal oxides are of the group alumina, zirconia and beryllia, other metal oxides may be present, generally in small percentage, in addition to one of the three stated oxides, as for instance manganese, copper, cobalt, nickel, iron, chromium, vanadium, thorium, titanium and molybdenum. Active synthetic catalysts may be prepared by any suitable method as by coprecipitation of the silica and metal oxide, by separate precipitation and blending, or by the precipitation of one upon a suspension of the other. The best catalysts are substantially free of sodium and other alkali metals, containing less than 1% of alkali metal oxide computed on the basis of sodium oxide equivalent. Suitable methods of preparing such synthetic catalysts are disclosed in my copending applications Serial Nos. 310,762 and 410,165. The present invention, however, is not limited to catalysts prepared by particular methods, but is of general application to silicious cracking catalysts. While in some respects the natural and synthetic silicious cracking catalysts are not fully equivalent, the two types appear in the present relationship to be substantially full equivalents and to be affected in generally the same manner.

The conditioning of the catalyst is effected by a treatment with steam at a partial pressure of at least three-tenths of a pound per square inch, at an elevated temperature between 800 and 1650° F. The steam pressure employed, in general, varies inversely as the temperature, and should be correlated with the temperature so as to lie within the zone between the lines AB and CD, as shown in the accompanying drawing. Within this zone the rate at which the activity of the catalyst is shifted from one type of activity to another type is relatively rapid so a short treating time may be used, on the order of a day or less, and yet sufficiently slow that the time does not become so short that accurate control of the result is not obtainable. The lines AB and CD have been determined purely on a basis of the results obtained in the conditioning of catalysts. In order to determine accurately whether a given set of conditions lies within or without this zone, empirical mathematical expressions for these two lines have been determined. The partial pressure of steam expressed in lbs. per sq. in. is equal to

$$\frac{35.4 \times 10^6}{T^2} - 20.6$$

along the line AB, and

$$\frac{250 \times 10^6}{T^2} - 92$$

along the line CD, when T is the temperature of the treatment expressed in degrees Fahrenheit. It should be remembered that these two equations are purely empirical and based upon result and not upon theory.

The rate at which the preconditioning occurs and the degree to which the catalyst is affected are dependent, to a major extent, upon the selected conditions of treatment and upon the purity of the catalyst being treated. Thus, conditions toward the line CD are increasingly severe with resulting increase of rate, while conditions toward the line AB are milder with resulting decrease in rate. With relatively impure materials, such as synthetic catalysts of high alkali metal content, it is generally preferable to operate at conditions selected toward the line AB. More severe conditions are generally employed with the synthetic catalyst containing less than 1% alkali metal compounds. With activated clays, such as disclosed in the aforementioned Houdry patent, it is preferred that the temperature and pressure be correlated to fall below the line EF. Along the line EF the partial pressure of steam equals

$$\frac{81 \times 10^6}{T^2} - 36.3$$

In this range, below the line EF, very accurate reduplication of preconditioning is obtainable.

The severity of the treatment, i. e., the extent of modification of the catalyst, is accordingly a function both of the severity of treating conditions and of length of time the catalyst is treated. In accordance with this invention the catalyst is treated in the preconditioning step at least sufficiently that the ratio of gasoline to coke produced in cracking is increased 25%, and is limited sufficiently that the amount of gasoline produced is not decreased more than 20%. The actual extent of modification of the catalyst to effect this result varies considerably with the type of charge stock to be cracked.

The severity of the treatment of the catalyst

varies substantially with the stock to be cracked. The relationship of the severity of treatment to stock is as follows: the more refractory the stock to catalytic cracking, the milder should be the treatment; the less refractory the stock, the more severe should be the treatment. Thus, with a light gas oil a very limited treatment should be effected. The result of such a treatment is that the amount of gasoline produced is generally reduced slightly and in some instances is about the same or slightly increased under comparable cracking conditions. The amounts of gas and coke are reduced very substantially and the liquid recovery is considerably increased. The reduction of the amount of coke is so much greater in proportion to the reduction in the amount of gasoline that the ratio of gasoline to coke is increased more than 25%. When the stock to be cracked is a very heavy gas oil, often termed a "heavy residuum" from which the heavy tar has been removed, a much more severe treatment is used. The results obtained in comparative cracking tests are of the same character. With a heavy residuum the present invention is particularly noteworthy since the gasoline to coke ratio is generally increased on the order of 100%. This is an illustration of the point that the present procedure is probably not an actual poisoning of the catalyst but is a treatment which shifts the activity thereof.

It is in general preferred to operate at a partial pressure of steam below 100 lbs. However, if desired, suitable treating conditions can be selected at higher partial pressures of steam than 100 lbs. at temperatures above 800° F. and at partial pressures of steam below the line CD.

A special application of the present invention involves the preconditioning of synthetic silicious cracking catalysts for the cracking of naphthas and light gas oils boiling up to about 800° F. For such a charge it is preferred to effect a very mild conditioning of the catalyst such that the gasoline produced is decreased not more than 10%, which treatment is effected at a temperature of 1400° F. or higher and at a partial pressure of steam below 10 pounds. Catalysts of this variety are of great utility in the production of aviation gasolines, as disclosed in my copending applications Serial Nos. 365,923 and 365,924.

The range of conditions under which catalytic cracking is effected is known in the industry as is also the general type of operation. It is to be noted, however, that the present invention is applicable both to plants employing a stationary catalyst and alternate on-stream and regeneration periods, and to plants in which the catalyst moves in cycle through a cracking zone wherein it is on stream and through a regeneration zone wherein it is in regeneration. In many instances steam is used in direct contact with the catalyst during a portion of the cycle. In accord with a particular form of this invention the steam pressure and temperature during the cyclic cracking operations are correlated so that at all times the steam and temperature correlate at a point below the line AB. By this means the specific adjusted activity of the catalyst is maintained without substantial change for many months of use.

The present invention is more specifically illustrated in the following examples.

Example 1

Solutions of sodium silicate and sodium aluminate containing SiO_2 and Al_2O_3 in molar ratios

of about 12:1 were mixed to form a sol to which a sufficient quantity of ammonium sulphate was added to yield a gelatinous coagulum having a pH of the order of 9.5. After drying, the coagulum was treated with an ammonium chloride solution until its sodium oxide content was reduced to below 0.5% and was then heated to about 1050° F. for approximately two hours to dehydrate it and drive off ammonium. Portions of the catalyst so prepared were preconditioned under various temperatures and steam pressures for varying times, as shown in the accompanying table, and were employed for cracking a light East Texas gas oil fraction having an A. P. I. gravity of about 36° and a boiling range of about 440 to 720° F., at a catalyst temperature of 800° F., at atmospheric pressure and at a rate of 1½ volumes liquid charge per liter of catalyst per hour. The results obtained in cracking under these conditions with the catalyst not preconditioned and after preconditioning are shown in the table:

Portion	Steam treatment conditions			Cracking results		
	Temp., °F.	Steam press., (lb./sq. in. abs.)	Time, hrs.	410° F. E. P. gasoline per cent vol. of charge	Coke wt. per cent of chg.	Gas wt. per cent of charge
1	---	---	---	47	5.3	11
2	1,250	3	2	46.7	3.9	7.7
3	1,400	0.75	10	46.7	3.3	7.6
4	1,050	15	2	41.4	3.2	7.1
5	900	45	2	39.1	2.6	4.4
6	1,330	15	6	34.4	1.5	2.8
7	850	15	33½	32.6	1.6	3.4
8	1,350	15	6	29.6	1.2	2.4
9	1,300	45	2	25.7	0.9	1.2
10	1,300	75	2	20.6	0.6	1.3

It is to be noted that for the cracking of this type of stock the preconditioning of portions 2 to 5 produced advantageous results, whereas the preconditioning of portions 6 to 10 was so severe that for this type of stock these catalysts were unsuitable. The gasoline to coke ratio of portion 1 was 9.05. The ratios of portions 2 to 5 were respectively: 12., 14., 13., and 17., which shows that the increases ranged between 30% and 90% in these instances.

Portions 1 and 6 were employed for the cracking of a heavy residuum of an East Texas crude prepared by removal of the initial 56% of the crude and 12% of the heavy ends, which heavy residuum had an initial boiling point of about 550 and an end point of about 1000° F., the remainder being sufficiently high boiling that it was impossible to determine the range. The cracking was performed at a rate of twenty volumes liquid basis of the charge per volume of catalyst per hour, at a temperature of 835° F., a pressure of 7 lbs./sq. in. and in the presence of 20% steam. The comparative results are shown in the following table:

Portion	Steam treatment conditions			Cracking results		
	Temp., °F.	Steam press., (lb./sq. in. absolute)	Time, hrs.	410° F. E. P. gasoline per cent vol. of charge	Coke wt. per cent of chg.	Gas wt. per cent of chg.
1	---	---	---	46.3	7.7	22.2
6	---	15	6	41.2	2.9	14.1

By the steam treatment of portion 6, while the treatment was too severe for light gas oil, for a

heavy stock, as shown, very advantageous results are produced. Further, it is interesting to note that in cracking the heavy stock, the liquid recovery was increased from 76.3 for portion 1, to 88.8 for portion 6.

Portion 9, which likewise was treated too severely for the cracking of light stock, was utilized for transforming high sulphur crude from Santa Maria field in California into high octane motor fuel. In this operation the entire crude, which had an A. P. I. gravity of about 15.7 was rapidly heated to about 900° F. in the presence of about 20% by weight of steam and the resulting vapors were separated from unvaporized material. These two steps were conducted under such conditions, including high rate of feed and low pressure, as to minimize thermal cracking into gasoline and gas. The vapors, making up about 99.4% of the original crude, were passed over catalyst identified as portion 9, at a pressure of about 8 lbs. per sq. in. gage and a rate of about 3 volumes of charge per volume of catalyst per hour. There was thereby obtained 46% by volume based on charge of 400° F. end point motor fuel, with the concomitant production of 3.4% by weight of coke and 2.6% by weight of gas. There was also obtained 54% by volume of a clean recycle stock having an A. P. I. gravity of 20°.

Example 2

An activated clay was employed as a catalyst and had the following approximate composition:

Silica	67.06
Alumina	15.73
FesO ₃	2.63
Ca oxide	1.36
Mg oxide	4.17
Na ₂ O	.57
Moisture	16.07
Ignition loss	8.16

This catalyst was tested in the cracking of a heavy residuum from East Texas crude as described in Example 1, the cracking being conducted at a rate of 1 volume liquid basis of feed per volume of catalyst per hour, at a catalyst temperature of 850° F., under a pressure of 7 lbs. per sq. in. gage with 15% steam. Under these conditions a liquid recovery of 75.4% by volume of charge was obtained, which yielded 43% by volume gasoline, based on charge. Gas was produced during the cracking to the extent of 22% by weight of the charge and coke was laid down on the catalyst to the extent of 8.2% by weight of the charge. Clay of this type was treated with steam at a partial pressure of 15 lbs. for 6 hours at 1330° F. The same charge stock was cracked under identical conditions. With the catalyst so treated the liquid recovery was increased to 93%, the gasoline to 44%, while the gas was decreased to 9.9% and the coke to 4.2%. The ratio of gasoline to coke with the untreated catalyst was 5.25, whereas with the treated catalyst the ratio was 10.5, an increase of 100% in the ratio.

A similar clay catalyst was employed for the cracking of a light East Texas gas oil under the conditions stated in Example 1, whereby there was produced a yield of 40.9% by volume of gasoline, 3.9% by weight of coke and 5.1% by weight of wet gas. Catalyst of this character was steam treated at 1150° F. for four hours at a partial pressure of steam of 15 lbs. per sq. in. When employed for cracking a light East Texas gas oil under identical conditions a yield of 34.5% by volume of gasoline was obtained, with the pro-

duction of 2.6% by weight of coke and 2.4% by weight of gas. The ratio of gasoline to coke was increased about 25% by the treatment.

Example 3

A silica zirconia synthetic cracking catalyst was prepared by forming a sol of zirconium sulphate and sodium silicate containing SiO_2 and ZrO_2 in molar ratio of 15.1 to 0.755, enough sulphuric acid being added to bring the pH to 6.0. The precipitated material was dried, washed, treated with ammonium chloride to free it of sodium, following which the catalyst was hardened at 1050°F . for two hours in air. When employed for the cracking of a light East Texas gas oil under the conditions stated in Example 1, a yield of 47.3% gasoline by volume was obtained, with the production of 6% by weight of coke and 4.2% by weight of gas, which had a specific gravity of 1.35. The catalyst was steam treated at 1400°F . for 10 hours in 5% steam. The finished catalyst, so treated, when employed for cracking light East Texas gas oil under the same conditions, produced a yield of 38.8% gasoline, 2.1% coke and 2.0% gas of 1.07 specific gravity. Thus it is to be seen that the steam treatment effected a reduction of only 18% in the gasoline produced on a once-through basis, but effected an increase of 134% in the ratio of gasoline to coke.

The present application is a continuation of my copending application Serial No. 289,915, filed August 12, 1939.

What I claim is:

1. The process which comprises catalytically cracking a hydrocarbon charge stock heavier than gasoline in the presence of an active silicious cracking catalyst which has been preconditioned for the cracking of said charge stock by subjecting the catalyst to contact with steam at a partial pressure above 0.3 pound per square inch and a temperature between 800°F . and 1650°F ., the partial pressure of steam being correlated with the temperature to lie between the lines AB and DC in the accompanying drawing and for a time sufficient to increase the gasoline to coke ratio at least 25% and insufficient to effect a decrease of more than 20% in the gasoline produced in the cracking of said charge stock.

2. The process which comprises preconditioning an active silicious cracking catalyst for the catalytic cracking of a selected type of heavier than gasoline charge stock by subjecting the catalyst to contact with steam at a partial pressure above 0.3 pound per square inch and a temperature between 800°F . and 1650°F ., the partial pressure of steam being correlated with the temperature to lie between the lines AB and CD in the accompanying drawing and for a time sufficient to increase the gasoline to coke ratio at least 25%, and insufficient to effect a decrease of more than 20% in the gasoline production in the cracking of the selected type of charge stock.

3. The process which comprises the steps of preconditioning an active silicious cracking type of catalyst for the conversion of a selected type of hydrocarbon charge stock under conditions that gasoline boiling range materials are contained in the effluent product and coke-like material is deposited in the catalyst, by subjecting the catalyst to contact with steam at a partial pressure above 0.3 pound per square inch and a temperature between 800°F . and 1650°F ., the partial pressure of steam being correlated with the temperature to lie between the lines AB and CD in the ac-

companying drawing and for a time sufficient to increase the gasoline to coke ratio at least 25% and insufficient to effect a decrease of more than 20% in the gasoline in the effluent product of conversion of said hydrocarbon charge stock, and subjecting said hydrocarbon charge stock to said conversion in contact with the catalyst so preconditioned.

4. The process which comprises the steps of preconditioning an active silicious cracking catalyst for the catalytic cracking of a selected type of heavier than gasoline charge stock by subjecting the catalyst to contact with steam at a partial pressure above 0.75 pound per square inch and a temperature between 800°F . and 1650°F ., the partial pressure of steam being correlated with the temperature to lie between the lines AB and CD in the accompanying drawing and for a time sufficient to increase the gasoline to coke ratio at least 25% and insufficient to effect a decrease of more than 20% in the gasoline production in the cracking of the selected type of charge stock, and catalytically cracking the selected type of stock in the presence of the catalyst so preconditioned.

5. The process which comprises the steps of preconditioning an active silicious cracking catalyst for the catalytic cracking of a selected type of heavier than gasoline charge stock by subjecting the catalyst to contact with steam at a partial pressure above 0.3 pounds per square inch and a temperature between 800°F . and 1650°F ., the partial pressure of steam being correlated with the temperature to lie between the lines AB and CD in the accompanying drawing and for a time sufficient to increase the gasoline to coke ratio at least 25% and insufficient to effect a decrease of more than 20% in the gasoline production in the cracking of the selected type of charge stock, and catalytically cracking the selected type of stock in the presence of the catalyst so preconditioned.

6. The process which comprises the steps of preconditioning an active silicious cracking catalyst for the catalytic cracking of a selected type of heavier than gasoline charge stock by subjecting the catalyst to contact with steam at a partial pressure above 0.3 pound per square inch and a temperature between 800°F . and 1650°F ., the partial pressure of steam being correlated with the temperature, the partial pressure in pounds per square inch being greater than

$$\frac{35.4 \times 10^6}{T^2} - 20.6$$

and less than

$$\frac{250 \times 10^6}{T^2} - 92$$

when T is equal to the temperature in degrees Fahrenheit and for a time sufficient to increase the gasoline to coke ratio at least 25% and insufficient to effect a decrease of more than 20% in the gasoline production in the cracking of the selected type of charge stock, and cracking the selected type of stock in the presence of the catalyst so preconditioned.

7. The process defined in claim 6 in which the preconditioned catalyst during the cracking step is alternately employed on stream for cracking and subjected to regeneration, and maintaining the partial pressure of steam in pounds per square inch throughout on-stream and regeneration at less than

$$\frac{35.4 \times 10^6}{T^2} - 20.6$$

not yet
examined

when T is equal to the catalyst temperature in degrees Fahrenheit at the time of contact with steam.

8. The process which comprises the steps of preconditioning an active silicious gel type cracking catalyst for the cracking of low boiling hydrocarbon material heavier than gasoline for the production of gasoline by subjecting the catalyst to contact with steam at a partial pressure of steam

between 0.3 and 10 pounds per square inch and at a temperature above about 1400° F. and below the line CD correlated with the steam pressure as shown in the accompanying drawing, and cracking a low boiling heavier than gasoline hydrocarbon material in the presence of the catalyst so preconditioned.

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CERTIFICATE OF CORRECTION.

Patent No. 2,375,757.

May 15, 1945.

JOHN R. BATES.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 35, after "vanadium," insert "--tungsten,--"; page 3, second column, line 67, for "Eaxample" read "--Example--"; 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 11th day of September, A. D. 1945.

Leslie Frazer

(Seal)

First Assistant Commissioner of Patents.

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