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OXIDATION OF FATTY SUBSTANCES

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1

This invention relates to the oxidation of secondary-hydroxylated fatty substances to form keto fatty substances, and particularly to the oxidation of secondary-hydroxy fatty acids to form the corresponding keto acids.

Heretofore secondary-hydroxylated fatty acids have been oxidized to form the corresponding keto acids by treatment with glacial acetic acid and chromic anhydride, the glacial acetic acid acting as a solvent to dissolve the fatty materials and chromic anhydride to form a single-phase reaction medium. It is necessary to carefully restrain the progress of this reaction by means of artificial cooling, dilution and the like, in order to avoid oxidative scission of the fatty compound. This renders the process difficult to control, especially when commercial-size batches are made. Such processes are further not economical in that the considerable amounts of glacial acetic acid employed therein are completely lost.

Accordingly, it is an object of this invention to provide a readily-controlled process for converting hydroxylated fatty substances to the corresponding keto substances.

Another object is to avoid, or at least greatly reduce, the consumption of glacial acetic acid in the conversion of hydroxy fatty compounds to the corresponding keto compounds.

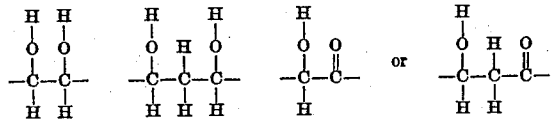
A further object is to obtain commercially practical yields of polyketo fatty substances by the oxidation of polyhydroxy fatty materials.

The above and other objects are achieved by this invention in a process which involves treating a saturated secondary-hydroxylated fatty material with an aqueous chromic acid solution at moderate temperatures so as to oxidize the hydroxy groupings in the fatty material to form keto groupings. The water contained in the aqueous chromic acid solution causes the formation of two separate phases, one containing the chromic acid, and the other containing the fatty material, thus effectively regulating the progress of the reaction and avoiding oxidative scission of the fatty material even at somewhat elevated temperatures. During the course of the reaction, the mixture is vigorously agitated to bring about intimate contact of the chromic acid and fatty-material phases. When the reaction is completed, the resulting keto fatty materials are separated from the spent chromic acid solution and are purified.

As starting materials in the process of this invention, there may be employed any fatty acids containing secondary-hydroxylated fatty chains of 8 or more carbon atoms; alkyl, aryl or aralkyl

2

esters of such acids; amides and substituted amides of such acids; and secondary fatty alcohols containing 8 or more carbon atoms; or any mixture containing one or more compounds of the types just indicated as suitable. The fatty chains contained in the starting materials to be processed in accordance with this invention may contain one or more hydroxyl groups, which may be distributed along the chains in practically any configuration. Those mono- and poly-hydroxylated materials which do not contain any of the labile groupings:



will result in practically quantitative yields of the corresponding keto substances. Starting materials containing one of the above groups will result in somewhat reduced yields of keto fatty substances, since the keto compounds resulting from the oxidation of the hydroxyl groups in these configurations tend to be oxidatively and/or hydrolytically split in the vicinity of the keto groups. Starting materials containing two or more of the above-listed groups will, of course, result in relatively low yields.

Hydroxylated fatty acids suitable for use as starting materials in the practice of this invention are exemplified in 12-hydroxystearic acid; 10-hydroxystearic acid; 9-hydroxystearic acid; 9- and 10-hydroxypalmitic acids; 9- and 10-hydroxymyristic acids; 9,10- and 10,12- and 9,12-dihydroxystearic acids; 9,10-dihydroxypalmitic acid; and many other like acids. Likewise suitable are the esters of the above acids with mono- and polyhydroxy alcohols, such as the methyl, ethyl, propyl, butyl etc. alcohols; ethylene and propylene glycols and polyglycols; glycerine; the "cellosolves"; and pentaerythritol. Other suitable compounds include the fatty alcohols, ethers and amides corresponding to the hydroxylated fatty acids of the types above set forth as being amenable to the process of the invention. Instead of the pure acids, esters and the like, there may be employed mixtures containing compounds coming within the requirements above set forth, such as natural hydroxylated fatty materials on the order of hydrogenated castor oil and the acids, esters, alcohols, ethers and amides derived therefrom; or fatty materials which have been processed—for example, by wet-blowing, or sulfonation and hydrolytic desulfonation—to develop hydroxyl groups therein, such as wet-blown cot-

tonseed oil, corn oil, sardine oil and the like, or sulfonated and hydrolytically desulfonated olive oil, castor oil, sperm oil, teaseed oil, peanut oil, oleic acid and the like.

Referring to the aqueous chromic acid oxidizing reagent, this may conveniently be an aqueous solution of $Na_2Cr_2O_7$ and H_2SO_4. However, the chromic acid solution may be prepared from any other hexavalent chromium compound such as CrO_3, $K_2Cr_2O_7$ or Na_2CrO_4 and any other oxidation-stable mineral acid such as HNO_3 or H_3PO_4. The water content of the oxidizing reagent must be sufficiently high to cause the chromic acid to form a separate phase when mixed with the hydroxylated fatty material. In general, the amount of sulfuric acid contained in the oxidizing reagent should be between about 25% and about 75% of the combined amounts of water and sulfuric acid present therein. The hexavalent chromium compound should be present in approximately 10% excess over the quantity stoichiometrically required to oxidize the fatty material to be treated; however, in those cases in which side reactions are to be expected—for instance in the treatment of materials containing the labile groups listed above, the excess should be increased to 50% or higher. The optimum proportions are best determined by preliminary experiment on the particular fatty material to be processed, bearing in mind the general considerations above set forth.

In addition to the chromic acid, the oxidizing mixture may also have incorporated therewith a small amount of an oxidation-resistant mutual solvent for the fatty material and the chromic acid, such as acetic acid. However, in contrast to the prior practice, the solvent is used in a relatively small amount, insufficient to cause the aqueous and fatty-material phases to merge.

Referring to the oxidation process, this is carried out by intimately mixing and agitating the hydroxylated fatty starting material with the aqueous chromic acid solution. The agitation is continued throughout the duration of the reaction to avoid local stagnation and to insure contact between the aqueous chromic acid phase and the fatty starting material. The temperature is maintained sufficiently high to effect the oxidation of the hydroxyl groups in the fatty materials to keto groups at an economic rate, but is not maintained so high as to cause oxidative scission of the fatty chains. In general, temperatures between about 20° and about 80° C. will accomplish these results, depending on the nature of the fatty starting material. This is in contrast with earlier procedures, wherein the temperature had to be carefully and skillfully moderated to avoid oxidative scission and other side-reactions. The length of time required for the completion of the reaction will vary with the nature of the starting material, the composition of the oxidizing agent, and the temperature at which the reaction is conducted. In general, between about 5 and about 8 hours will be required.

At the conclusion of the oxidation reaction, the reaction mixture is diluted with water and the oxidized fatty material is separated from the spent acids and salts. Thereafter the occluded acids and salts are washed out of the oxidized fatty product by means of aqueous washing solutions, and the washed product is recrystallized by means of organic solvents. The aqueous washing agent should preferably be slightly acid, in order to prevent the formation of, and to break up, any complexes or soaps formed by the fatty material with the chromic ions resulting from the oxidation reaction.

The practice of this invention as above outlined results in excellent yields of ketonic fatty products free of undesired by-products. The ketonic fatty products which are recovered are characterized by sharp melting points. Certain of the products made in accordance with this invention as described hereinbelow have previously been made by other processes; in all such cases, the melting points and other properties of the products agree with the data heretofore published.

Specific examples of the practice of this invention will now be described, all parts given being by weight. The sodium dichromate referred to in the examples was in all cases the hydrate $Na_2Cr_2O_7 \cdot 2H_2O$.

Example I

12-ketostearic acid

30 parts of the fatty acids derived from hardened castor oil, 45 parts of concentrated sulfuric acid, and 40 parts of water were stirred together to form a suspension and the temperature of the suspension was adjusted to 45° C. While continuing the stirring, a solution of 15 parts of sodium dichromate in 20 parts of water was slowly added at such a rate that the temperature of the mixture was maintained below 45° C. Stirring was continued for a total of 8 hours, after which the mixture was diluted with an excess of water and the solids were removed from the liquids by filtration. The solid products remaining on the filter were washed with water to remove the inorganic material therefrom. The solid products were then boiled for 1 hour with 60 parts of 18% aqueous hydrochloric acid solution. The dilute acid solution was removed and replaced with water and the boiling continued for another hour. The fatty materials were allowed to solidify, and were then separated from the liquids by filtration. The crude product, amounting to 30 parts, was dried. The crude product was twice recrystallized from ligroin (B. P. 73° to 126° C.) to yield 22 parts of substantially pure 12-ketostearic acid melting between 81.5° and 82.5° C. This material was readily converted to a semicarbazone which melted between 122.5° to 124° C.

Example II

12-ketostearic acid

Batches of hydrogenated castor oil fatty acids were treated exactly as described in the preceding example, with the exception that the quantities of reagents, times, and temperatures of reactions were varied. The conditions of treatment of the several batches, and the quantities and properties of the resultant yields, are tabulated herewith:

Reagents (parts by weight)				Reaction		Pure product	
Hydrogenated castor oil fatty acids	H_2SO_4	H_2O	$Na_2Cr_2O_7 \cdot 2H_2O$	Time, hrs.	Temp., °C.	Yield, Parts by weight	Melting Point, °C.
[1] 30	45	60	15	8	45	7	81–82
39	92	300	22	8	45	29	75.5–77.3
30	45	60	15	24	35	22	80–82

[1] Inferior grade of hydrogenated castor oil fatty acids having neutral equivalent of 1190 was employed in this reaction. 11 parts of glacial acetic acid were incorporated into the reaction mixture.

Example III

Glycerides of 12-ketostearic acid

31 parts of finely powdered hardened castor oil (acid value 6.0, acetyl value 130,) 200 parts of concentrated sulfuric acid and 150 parts of water were stirred together to form a suspension, and the temperature of the suspension was adjusted to 70° C.±5° C. While the stirring was continued, a solution of 30 parts of sodium dichromate and 50 parts of water was added at such a rate as to maintain the temperature at 70° C.±5° C. Stirring was continued at 70° C.±5° C. for a total of 8 hours, after which the solids were separated from the liquids by filtration. The solid products remaining in the filter were washed with water to remove the inorganic material therefrom. The solid products were then boiled for ½ hour with 60 parts of 18% aqueous hydrochloric acid solution. The dilute acid solution was removed and replaced by water and the boiling continued for an additional half hour. After allowing the fatty material to solidify by cooling, the solids were separated from the liquid by filtration. The crude product, amounting to 30 parts, was dried. This consisted largely of the glycerides of 12-ketostearic acid. The product possessed the following properties: acid value 6.0, saponification value 185, acetyl value 0. By saponification with alcoholic potassium hydroxide, an acid which melted in the range 81.5°–82.5° C. was isolated. The neutral equivalent of this acid was 297. It yielded a semicarbazone melting in the range 123°–124.5° C.

Example IV

Glycerides of 12-ketostearic acid

31 parts of finely powdered hardened castor oil (acid value 6.0, acetyl value 130), 250 parts of water and 305 parts of concentrated sulfuric acid were stirred together to form a suspension, and the temperature of the suspension was adjusted to 35°±5° C. While the stirring was continued, a solution of 117 parts of sodium dichromate in 150 parts of water was slowly added at such a rate that the temperature was maintained below 35° C. Stirring was continued for a total of 16 hours at 35° C.±5° C., after which the solids were removed from the liquids by filtration. The solid products remaining in the filter were washed with water to remove the inorganic material therefrom. The solid products were then boiled for ½ hour with 60 parts of 18% aqueous hydrochloric acid solution. The dilute acid solution was removed and replaced by water and the boiling continued for another ½ hour. The fatty material was allowed to solidify by cooling, and the resultant solids were separated from the liquids by filtration. The crude product, amounting to 31 parts, was dried and recrystallized from ligroin (B. P. 73°–126° C.) once. The purified product, which consisted largely of glycerides of 12-ketostearic acid, possessed the following properties: acid value 11.0, saponification value 189, acetyl value 45, melting point 81.5° to 82.5° C. By saponification with alcoholic potassium hydroxide, an acid which melted from 80°–81° C. was isolated. This acid yielded a semicarbazone melting from 120°–123° C.

Example V

Methyl esters of 12-ketostearic acid

31 parts of the methyl esters of hardened castor oil fatty acids (acid value 0, saponification value 183, acetyl value 137), 60 parts of water and 45 parts of concentrated sulfuric acid were stirred together to form a suspension, and the temperature of the suspension was adjusted to 45° C. While continuing the stirring, a solution of 13 parts of sodium dichromate in 20 parts of water was slowly added at such a rate that the temperature of the mixture was maintained at 45°±5° C. The stirring was continued for a total of 8 hours, after which the mixture was diluted with an excess of water and the solids were removed from the liquids by filtration. The solid products were then boiled for ½ hour with 60 parts of 10% aqueous hydrochloric acid solution. The dilute acid solution was removed and replaced with water and the boiling continued for ½ hour. After allowing the fatty material to solidify by cooling, the solids were separated from the liquids by filtration. The crude solid product, amounting to 31 parts, was dried. This consisted largely of the methyl esters of stearic acid and 12-ketostearic acid. The product exhibited the following properties: acid value 7.0, acetyl value 7.0, saponification value 181. It melted between 39° and 45° C. Saponification with aqueous sodium hydroxide yielded an acid melting in the range from 82°–83° C., with a neutral equivalent of 300.

Example VI

Mixed 9- and 10-ketostearic acid

30 parts of a mixture of 9- and 10-hydroxy stearic acid prepared by hydrolysis of sulfated red oil, 45 parts of concentrated sulfuric acid and 60 parts of water were stirred together to form a suspension, and the temperature of the suspension was adjusted to 45° C. With continued stirring, a solution of 15 parts of sodium dichromate in 20 parts of water was slowly added at such a rate that the temperature of the mixture was maintained at 45°±5° C. The stirring was continued for a total of 6 hours, after which the mixture was diluted with an excess of water and the solids were removed from the liquids by filtration. The solid products remaining on the filter were washed with water to remove inorganic materials therefrom. The solid products were then boiled for 1 hour with 18% aqueous hydrochloric acid solution. The dilute acid solution was removed and replaced with water and the boiling continued for another hour. After allowing the fatty material to solidify by cooling, the solids were separated from the liquids by filtration. The crude product, amounting to 29 parts, was dried. The crude product was twice recrystallized from ligroin (B. P. 73°–126° C.) to yield 22 parts of product melting from 62°–69° C., with a neutral equivalent of 302.

Example VII

Mixed 13- and 14-ketobehenic acids

35 parts of mixed 13- and 14-hydroxy behenic acids (M. P. 78°–83° C., N. E. 366), 45 parts of concentrated sulfuric acid and 70 parts of water were stirred together to form a suspension, and the temperature of the suspension was adjusted to 65° C. While continuing the stirring, a solution of 15 parts of sodium dichromate in 20 parts of water was slowly added at such a rate that the temperature of the mixture was maintained below 65° C. Stirring was continued for a total of 7 hours at 65° C.±5° C., after which the mixture was diluted with an excess of water and the solids were removed from the liquids by filtration. The solid products remaining on the filter were

washed with water to remove the inorganic material therefrom. The solid products were then boiled for 1 hour with 60 parts of 15% aqueous hydrochloric acid solution. The dilute acid solution was removed and replaced with water and the boiling continued for another hour. After allowing the fatty material to solidify by cooling, the solids were separated from the liquids by filtration. The crude product, amounting to 35 parts, was dried and recrystallized from ligroin (B. P. 78°–126° C.) to yield 29 parts of a mixture consisting essentially of 13- and 14-ketobehenic acids, melting in the range 70°–75° C.

EXAMPLE VIII

13,14-diketobehenic acid

30 parts of 13,14-dihydroxy behenic acid (obtained by the treatment of erucic acid with hydrogen peroxide and acetic acid) were suspended in 160 parts of 45% aqueous sulfuric acid solution and a solution of 27 parts of sodium dichromate in 40 cc. of water was added with stirring. The reaction did not proceed at 30°±5° C. At 45°±5° C. the reaction proceeded satisfactorily in 7 hours, after which the reaction mixture was poured into water and an oily layer separated therefrom. After the oily layer was separated from the aqueous phase, it was freed of lower mono-basic fatty acids by steam distillation.

The oily residue, amounting to 17 parts, left after steam distillation, was extracted with hot 18% aqueous hydrochloric acid solution to remove chromic compounds. After separation of the oil from the aqueous acid phase, it was extracted with ligroin (B. P. 73°–126° C.). The residue after recrystallization from acetone, amounting to 4 parts, was substantially pure brassidic acid (M. P. 112°–113° C.).

After removal of the ligroin from the above extracts, the residue, amounting to 12 parts, was isolated. This residue was recrystallized from ethyl alcohol to yield 6 parts of an acid (M. P. 93°–94° C. and neutral equivalent 368). This acid was essentially pure 13,14-diketobehenic acid.

EXAMPLE IX

Diketo acids derived from hydrolyzed sulfated castor oil

32 parts of the mixture of the dihydroxy stearic acids prepared by hydrolysis of sulfated castor oil fatty acids was suspended with stirring in a solution of 92 parts of concentrated sulfuric acid in 119 parts of water, and the temperature was adjusted to 45° C. While continuing the stirring, a solution of 66 parts of chromic anhydride in 70 parts of water was added at such a rate as to maintain the temperature below 45° C. Stirring was continued for a total of 7½ hours after which the reaction mixture was poured into water, whereupon an oily layer separated therefrom. Inorganic material and certain degradation products were extracted from this oily layer by three successive portions of hot water. The residual oil was freed of low molecular weight water-insoluble monobasic fatty acids by steam distillation. The residual semi-solid, which amounted to 11.5 parts, was recrystallized twice from ligroin (B. P. 73°–126° C.), to yield 2.5 parts of an acid melting from 91°–93° C. and having a neutral equivalent of 314.

EXAMPLE X

9,10-Diketostearic acid

32 parts of 9,10-dihydroxystearic acid (M. P. 89°–91° C.) were suspended with stirring in 179 parts of 45% aqueous sulfuric acid and to this suspension a solution of 33 parts of sodium dichromate in 30 parts of water was slowly added, the temperature being maintained throughout between 22° and 28° C. The stirring was continued for a total of 8 hours at this temperature, after which the reaction mass was poured into water and an oily layer separated therefrom. Inorganic materials and dibasic acids were extracted from this oily layer by three successive portions of hot water. The residual oil was freed of low molecular weight fatty acids by steam distillation. The residual semi-solid, which amounted to 145 parts, was recrystallized twice from ligroin (B. P. 73°–126° C.) There were obtained 9 parts of a yellow solid melting between 83°–84.3° C. and having a neutral equivalent of 308. This was essentially pure 9,10-diketostearic acid.

From the foregoing examples it will be seen that this invention provides a method for oxidizing hydroxy fatty materials to the corresponding keto compounds which is readily carried out and easily controllable at room, or even somewhat elevated, temperatures. Unusually high yields are obtainable by the process of this invention, which process, moreover may be applied to highly sensitive materials, such as the polyhydroxy fatty materials, to obtain commercial yields of the polyketo compounds. Finally, it is possible with this process to reduce or entirely eliminate the use of the glacial acetic acid solvent heretofore required in oxidation processes of this sort.

We therefore claim:

1. A process which comprises reacting a saturated fatty material containing a secondary-hydroxylated acyl chain of at least 8 carbon atoms and of the group consisting of fatty acids and substantially completely esterified fatty acid esters of monohydric and polyhydric alcohols with a hexavalent chromium compound in the presence of an oxidation-resistant mineral acid and in the presence of sufficient water to insure maintenance of an aqueous phase separate from the fatty material.

2. A process which comprises reacting a saturated secondary hydroxylated fatty acid containing at least 8 carbon atoms with a hexavalent chromium compound in the presence of an oxidation-resistant mineral acid and in the presence of sufficient water to insure maintenance of an aqueous phase separate from the fatty material.

3. A process which comprises reacting a saturated secondary monohydroxy fatty acid containing at least 8 carbon atoms with a hexavalent chromium compound in the presence of an oxidation-resistant mineral acid and in the presence of sufficient water to insure maintenance of an aqueous phase separate from the fatty material.

4. A process which comprises reacting 12-hydroxy stearic acid with a hexavalent chromium compound in the presence of an oxidation-resistant mineral acid and in the presence of sufficient water to insure maintenance of an aqueous phase separate from the fatty material.

5. A process which comprises reacting a saturated fatty material containing 2 secondary-hydroxyl groups attached to an acyl chain of at least 8 carbon atoms and of the group consisting of fatty acids and substantially completely esterified fatty acid esters of monohydric and polyhydric alcohols with a hexavalent chromium compound in the presence of an oxidation-resistant mineral acid and in the presence of sufficient water to in-

sure maintenance of an aqueous phase separate from the fatty material.

6. A process which comprises reacting 13,14-dihydroxybehenic acid with a hexavalent chromium compound in the presence of an oxidation-resistant mineral acid and in the presence of sufficient water to insure maintenance of an aqueous phase separate from the fatty material.

7. A process which comprises reacting a saturated substantially completely esterified fatty acid containing as its fatty acid chain a secondary-hydroxylated acyl chain of at least 8 carbon atoms with a hexavalent chromium compound in the presence of an oxidation-resistant mineral acid and in the presence of sufficient water to insure maintenance of an aqueous phase separate from the fatty material.

8. A process which comprises reacting a saturated fatty triglyceride containing a secondary-hydroxylated acyl chain of at least 8 carbon atoms with a hexavalent chromium compound in the presence of an oxidation-resistant mineral acid and in the presence of sufficient water to insure maintenance of an aqueous phase separate from the fatty material.

9. A process which comprises reacting hydrogenated castor oil with a hexavalent chromium compound in the presence of an oxidation-resistant mineral acid and in the presence of sufficient water to insure maintenance of an aqueous phase separate from the fatty material.

10. A process which comprises reacting a saturated fatty material containing a secondary-hydroxylated acyl chain of at least 8 carbon atoms and of the group consisting of fatty acids and substantially completely esterified fatty acid esters of monohydric or polyhydric alcohols with a hexavalent chromium compound in the presence of an aqueous solution of an oxidation-resistant mineral acid, the mineral acid being present to the extent of between 25% and 75%, based on the total weight of mineral acid and of water present in the reaction mixture.

11. A process which comprises reacting a saturated secondary hydroxy fatty acid containing at least 8 carbon atoms with a hexavalent chromium compound in the presence of an aqueous solution of an oxidation-resistant mineral acid, the mineral acid being present to the extent of between 25% and 75%, based on the total weight of mineral acid and of water present in the reaction mixture.

12. A process which comprises reacting a saturated fatty triglyceride containing a secondary-hydroxylated acyl chain of at least 8 carbon atoms with a hexavalent chromium compound in the presence of an aqueous solution of an oxidation-resistant mineral acid, the mineral acid being present to the extent of between 25% and 75%, based on the total weight of mineral acid and of water present in the reaction mixture.

13. A process which comprises reacting a saturated fatty material containing as its fatty acid chain a secondary-monohydroxylated acyl chain of at least 8 carbon atoms and of the group consisting of fatty acids and substantially completely esterified fatty acid esters of monohydric or polyhydric alcohols with a hexavalent chromium compound in the presence of an aqueous solution of an oxidation-resistant mineral acid, the mineral acid being present to the extent of between 25% and 75%, based on the total weight of mineral acid and of water present in the reaction mixture.

14. A process which comprises reacting a saturated secondary dihydroxy fatty acid containing at least 8 carbon atoms with a hexavalent chromium compound in the presence of an aqueous solution of an oxidation-resistant mineral acid, the mineral acid being present to the extent of between 25% and 75%, based on the total weight of mineral acid and of water present in the reaction mixture.

15. A process which comprises reacting a saturated substantially completely esterified fatty acid containing a secondary-hydroxylated acyl chain of at least 8 carbon atoms with a hexavalent chromium compound in the presence of an aqueous solution of an oxidation-resistant mineral acid, the mineral acid being present to the extent of between 25% and 75%, based on the total weight of mineral acid and of water present in the reaction mixture.

16. Process according to claim 2, wherein the hydroxylated fatty acids are those derived from hydrogenated castor oil.

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Certificate of Correction

Patent No. 2,446,849. August 10, 1948.

DONALD PRICE ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 4, line 71, in the table, 8th column thereof, for "75.5–77.3" read *74.5–77.3*; column 10, line 36, claim 16, for the claim reference numeral "2" read *3*; 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 26th day of October, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.