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ANTIRING STICKING LUBRICATING COMPOSITION

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8 Claims. (Cl. 252—37.7)

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This invention relates to improved lubricants, and to a method for their preparation. More particularly, the invention pertains to the preparation and use of addition agents in lubricating oils. In one of its more specific embodiments, the invention covers a process for the preparation of certain compounds which, when added to lubricating oils, materially improve their quality, particularly when such compounded oils are used for the lubrication of engines of the compression ignition type.

As is well known, the usual lubricating oils, when subjected to certain conditions or use, such as in internal combustion engines of the Diesel type or in spark ignition engines wherein piston temperatures are very high, tend to form sticky carbonaceous deposits which, over varying periods of use, accumulate in the piston ring grooves, causing the rings to stick and become ineffective. This problem of the piston ring sticking has assumed considerable importance since the advent of high-speed Diesel engines, aviation gasoline engines, and the like. The principal reason for this ring sticking appears to be the lacquer and/or carbon formation during the use of the lubricating oils in such engines.

It has previously been discovered that this ring sticking action may be materially reduced by the addition to the oil of certain selected materials. Thus, it is known that certain naphthenic materials have been compounded with or added to lubricating oils, and have been used in such oils with varying degrees of success either to inhibit the formation of or to maintain in solution or suspension those materials which lead to the phenomenon of ring sticking. These naphthenic compounds, however, have been found to be unsuitable when used with certain types of lubricating oils. It is also known that the addition of small amounts of certain metal salts of alkylated aromatic hydroxymonocarboxylic acids, in which the carboxylic acid radical is directly attached to the ring, preferably in the ortho position to the hydroxy radical, when added to lubricating oils reduce ring sticking tendencies of such oils. However, many of the substances of this latter type are only partially satisfactory as anti-ring sticking agents and are difficult to dissolve in lubricating oils in effective quantities.

It is therefore the main object of this invention to obviate the above and other defects, and to provide a product or compound which possesses excellent lubricating properties and which, when added to lubricating oils, is readily soluble therein in sufficient amounts to provide excellent anti-

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oxidant and/or detergent properties. It is a further object of the invention to provide a novel class of compounds which may be dispersed or dissolved in lubricating oils, which compounds possess excellent anti-ring sticking properties.

It has now been discovered that the above and other objects may be attained by using as a lubricant, or preferably, as an addition agent to lubricating oils, products or compounds which are the polyvalent metal salts of the reaction products obtained by alkylating and polymerizing an aromatic compound containing one or more polar groups together with an excess of an unsaturated organic compound having at least one aliphatic double bond, said aromatic compound containing more than 4 carbon atoms per molecule. It has been also discovered that these products, when used as lubricants per se, or as addition agents to ordinary lubricating oils, are exceptionally effective in that the interiors of the cylinders of aircraft engines and Diesel engines remain clean. Additionally, the presence of these novel mixtures of the metal salts of alkylation and polymerization products in lubricants for internal combustion engines prevents or at least materially inhibits the deposition of carbonaceous products on the pistons and in the piston ring grooves, and also inhibits the sticking of the piston rings. Furthermore, there is a material decrease in wear when the novel mixtures of the present invention are employed as or in lubricants for the lubrication of the specified engines, this wear being normally caused by corrosion.

The mixtures comprising the lubricants or lubricant additives of the present invention are prepared by polymerizing and alkylating a mixture of certain unsaturated organic materials, and certain aromatic compounds containing polar groups, both described hereinafter, and subsequently forming the metal salts of the mixtures thus prepared.

The aromatic compounds containing polar groups may be, for example, aromatic carboxylic acids, aromatic hydroxy carboxylic acids, or hydroxylated aromatic compounds such as phenols, naphthols, etc. Aromatic carboxylic acids useful in forming the subject mixtures include both monobasic and polybasic acids of either mononuclear or polynuclear configuration. Typical mononuclear aromatic acids are benzoic acid, phenylacetic acid, beta-phenylpropionic acid, mesitylic acids, ethylbenzoic acid, gamma-phenylbutyric acid, trimethylbenzoic acid, and alpha or beta naphthoic acids. Dicarboxylic aromatic

acids include phthalic acid, xylidinic acids, and cumidinic acids.

Typical hydroxy aromatic acids include ortho- meta or para-hydroxybenzoic acid, 4-hydroxyphthalic acid-1,2, 4-hydroxy-1,3-dicarboxybenzene, 3-hydroxyphthalic acid-1,2, 2-hydroxy-1,3-dicarboxybenzene, 5-hydroxy-1,3-dicarboxybenzenes, etc.

Phenolic materials are useful in preparing the mixture of products useful in the compositions of the present invention. These include phenol, ortho-, meta-, and para-aminophenol, 2-amino-3-nitrophenol, resorcinol, catechol, ortho-, meta-, and para-anilinophenol, ortho-, meta-, and para-butoxyphenol, 2,3-dinitrophenol, etc.

As indicated above, the various aromatic compounds useful in forming the compositions of the present invention, may contain alkyl, aryl or aralkyl radicals, as well as alkoxy, aroxy, or amino groups, in addition to hydroxyl or carboxyl groups.

Aromatic substances of the classes indicated above are preferably condensed with the unsaturated olefinic materials in the presence of catalysts to form a mixture of alkylates and polymers. The unsaturated aliphatic material contains one or more olefinic linkages. Such materials include unsaturated aliphatic hydrocarbons, preferably having at least 4 carbon atoms. These include butylene, amylene, hexylene, heptylene, octylene, nonylene, decylene, cetene, cerotene, molene, etc. The cycloalkenes likewise are useful. These include cyclohexene and substituted cyclohexenes. Mixtures derived from natural products form preferred materials for use in the present invention. Such mixtures of alkenes include vapour or liquid phase cracking distillates of paraffin wax, unsaturated esters such as those found in rape seed oil and soya bean oil. Other suitable unsaturated materials include unsaturated alcohols such as allyl alcohol, unsaturated acids such as oleic acid, and unsaturated aldehydes such as acrolein.

The alkylation and polymerization of mixtures of the above components may be conducted concurrently or consecutively. Thus polymerization and alkylation may be effected simultaneously, or polymerization may follow alkylation, or alkylation may take place after polymerization. Simultaneous polymerization and alkylation is preferred.

Catalysts which promote the polymerization and alkylation of the subject mixtures are of the type represented by aluminum chloride, boron trifluoride and hydrofluoric acid. Promoters such as concentrated sulfuric acid or ortho-phosphoric acid may also be present, although they are not essential.

Although a solvent is not essential to the preparation of the mixtures, a substantially inert solvent may be used. Preferably such a solvent is a saturated hydrocarbon, or mixture thereof, such as a lubricating oil.

The reaction is usually conducted under reflux conditions, such that volatile constituents, including any lower olefinic materials present therein are returned to the reaction zone, while any gaseous materials, such as hydrogen or gaseous catalysts pass off and are collected for disposal or re-cycling.

The temperature of polymerization and alkylation of the mixture may vary within relatively wide limit. Preferably, when an active catalyst such as boron trifluoride is employed, the reaction temperature is from about 50° C. to about 200° C., optimum yield of polymer and alkylate being obtained when the temperature is from about 75° C. to about 125° C. A maximum amount of the aromatic component is alkylated when the temperature is between 100° C. and 125° C. while the utilization of the olefin, either in polymerization or alkylation, is increased as the temperature diminishes. Examples of the concurrent polymerization and alkylation are presented hereinbelow.

Alternatively, polymerization of an olefin or mixture of olefins may be initiated prior to the addition of the aromatic compound. Furthermore, the aromatic compound may be alkylated with an olefin, after which additional olefinic material (of either a similar or dissimilar identity) may be introduced, after which polymerization is allowed to take place.

The mixture formed by the alkylation and polymerization has free base-binding groups, the amount substantially dependent upon the amount of alkylated aromatic present therein. Since the effectiveness of the present mixture as a lubricant additive is primarily dependent upon the amount of base-binding group present, it is a preferred practice to adjust the reaction conditions so that a maximum amount of alkylated aromatic material is present in the mixture.

The time of polymerization and alkylation is dependent upon several factors such as the identity of the components and the catalyst, the reaction temperature and the product desired. When an active catalyst such as aluminum chloride or boron trifluoride is present, and the reaction temperature is from about 75° C. to about 125° C. optimum results are obtained when the reaction is allowed to proceed for about 2–20 hours, preferably from 3 to 8 hours.

After the polymerization and alkylation have been completed, the mixture may be purified by the removal of solvents, unreacted components and catalyst. For example, the mixture may be subjected to distillation or steaming for the removal of low boiling constituents, and then may be water-washed or otherwise treated to remove catalysts and other water-soluble components.

While the mixture of alkylate and polymerizate is useful as a lubricant additive, it is preferred that the mixture be treated to form polyvalent metallic salts. Of the polyvalent metals, the metals of the second, third, sixth and iron groups of the periodic table are particularly suitable, examples of these metals being magnesium, calcium, strontium, barium, zinc, tin, nickel, manganese, lead, copper, cobalt and aluminum. Of these metals, those of the second and third groups of the periodic table are preferable, calcium and zinc being typical examples of these metals.

In order to prepare the metal salt, the mixture of alkylates and polymerizates described hereinbefore is preferably mixed with an oxide or hydroxide of one or more of the above metals. This incorporation may take place prior to, during or following the addition of the mixture of the alkylate and polymerizate to the main lubricating oil. The preferred method of salt preparation is to incorporate the metallic oxide or hydroxide with the mixture of alkylate and polymerizate in the presence of moisture at a temperature from about 50° C. to about 125° C., preferably about 90° C. Any excess metallic oxide or hydroxide may then be removed by extraction or centrifuging.

Dependent upon the nature of the mixture and its intended purpose as a lubricating oil additive,

the amount of metal ions present may be sufficient to completely react with all base-binding groups of the mixture, or a partial neutralization may be allowed to take place. Alternatively the mixture may contain a slight excess of the metallic oxide or hydroxide.

The exact composition of the novel lubricant additives of this invention is not known at the present time, except that they differ in effectiveness as lubricant additives from mixtures of olefin polymers with metallic salts of alkylated aromatic compounds. The calcium salt of the mixture of alkylate and polymerizate obtained according to the present invention when using salicylic acid and cracked wax olefines as the reaction components, differs in its effectiveness as a lubricant additive from that of calcium diisopropylsalicylate mixed with a polymer of cracked wax olefins. It is apparent from this difference that the mixture of the present invention has some configuration not heretofore discovered.

Other compounds useful as lubricant additives and having metallic contents as high as about 30% may be prepared by heating the metallic salts formed as described hereinbefore, at temperatures from about 250° C. to about 300° C., preferably in the presence of an inert medium such as a lubricating oil. Under these conditions, an insoluble precipitate is formed which subsequently redissolves, evolution of gases, such as carbon dioxide, taking place in the meantime. The constitution of the reaction product is unknown, except that the decomposition proceeds so as to effect a loss of carbon, hydrogen and oxygen, to give products having unusually high metallic contents. These thermal decomposition products are highly effective anti-ring sticking compounds. Normally they are solids or semi-solids at room temperature.

The metallic salts of the present invention form effective lubricating oil additives even when present therein in very minor amounts. Preferably, the concentration of the salt in the lubricant is from about 0.5% to about 20%, but optimum results are obtained when the concentration if from about 1% to about 5%, by weight.

The lubricant in which the additive is employed may be any fluid having lubricating properties, such as mineral oils, synthetic lubricants, such as polymeric hydrocarbons, poly (alkylene oxides), poly (alkylene glycols), viscous esters such as 2-ethylhexyl sebacate, polymeric amides and amines, silicone polymers, etc.

The substituents of the aromatic material and the olefin are chosen so as to obtain a metallic salt dispersible in the lubricating medium. While it is preferable that the salt be substantially completely dissolved in the lubricant, it may alternatively be uniformly dispersed therein in the form of a colloidal suspension, if necessary with the aid of a dispersing agent.

Other additives may be present in the lubricant, such as anti-corrosion agents, extreme pressure agents, viscosity index improvers, pour point depressors, anti-oxidants and supplementary anti-ring sticking compounds.

In accordance with one phase of the present invention, it has been found that an unusual improvement in the performance of the subject salts is caused by the addition thereto of polyvalent metal salts of alkylphosphoric acids, such as calcium cetyl phosphate. The presence of from about 20% to about 100% (preferably 40-80%), based on the salts of the mixture of alkylates and polymerizates, greatly increases the effectiveness of the latter.

The following examples are presented to illustrate the preferred methods of preparation of the mixtures possessing the above-mentioned anti-ring sticking and other properties, as well as to illustrate the advantages obtained by using said mixtures in lubricating compositions:

EXAMPLE I

Sixteen parts by weight of an olefinic vapour-phase cracked wax distillate (boiling range 150–208° C.), 2 parts by weight of salicylic acid and 30 parts by weight of nitrobenzene were placed in a kettle provided with a reflux condenser, a thermometer and a stirrer. Two and one-half parts of aluminum chloride was added in small portions, while the mixture was heated at 70° C. After 8 hours the reaction mixture was cooled, acidified with 2 N hydrochloric acid, washed with water and steamed to remove catalyst and unconverted materials. The product was a dark viscous oil having an acid number of 22.7. The oil was heated with an excess of zinc oxide at 90° C. in the presence of 0.5 part of water for one-half hour. Excess zinc oxide was removed by centrifuging.

A mineral lubricating oil containing 1% of the zinc salt mixture was found to be very effective in maintaining internal combustion engines in a clean condition.

EXAMPLE II

Sixteen parts by weight of mixed olefins, obtained as the distillate of vapour phase cracked wax (boiling range 30–340° C.), 2 parts salicyclic acid, 1.4 parts boron trifluoride and 6.6 parts phosphoric acid were heated at 125° C. for 3 hours, then washed with water and steamed. The product was heated at 90° C. with calcium hydroxide in order to form the calcium salt of the mixture of the alkylate and polymerizate formed in the above reaction. The calcium salt of the mixture proved to be an efficient anti-ring sticking additive for lubricating oil.

EXAMPLE III

Sixteen parts by weight of olefins, obtained as a distillate from the vapour phase cracking of paraffine wax, and two parts by weight of salicylic acid were heated for three hours with stirring, an excess of boron trifluoride being continuously introduced. Five runs were made using various temperatures and with the formation of the following products:

Table 1

Reaction Temperature	Yield, parts	Per Cent Salicylic Acid Alkylated	Per Cent Olefins Converted
50° C.	14.1	10	87
75° C.	13.1	48	76
100° C.	12.7	65	71
125° C.	12.1	62	68
150° C.	11.9	54	68

The products were dark oils which were purified by water washing and steaming. Zinc and calcium salts were prepared as described in Examples I and II.

EXAMPLE IV

Twenty parts of zinc salt prepared from the mixture obtained as described in Example III (reaction temperature 100° C.) and 80 parts by weight of a highly refined paraffine hydrocarbon

oil having a boiling range from 80° C. to 170° C. at 0.05 mm. of mercury pressure, were placed in a kettle provided with a stirrer and a condenser. The solution was rapidly heated while being stirred. At a temperature of about 220° C. and above a gas was evolved and a precipitate started to form, which precipitate redissolved at about 280° C. The dark solution was heated at 300° C. for one-half hour, at the end of which time the evolution of gas ceased. The product was steamed and the mineral oil removed by distillation, leaving an indeterminant mixture of zinc salts soluble in lubricating oils and possessing superior anti-ring sticking properties.

EXAMPLE V

Eighty parts by weight of mixed olefins, obtained as the vapour phase cracked distillate of paraffine wax, and having a boiling range of 30–340° C., and 10 parts phenol were heated at 100° C. under reflux while maintaining an excess of boron trifluoride. After 3 hours the product was purified by water washing and steam, and then was converted to the calcium salt as described in Example II. The product was an efficient anti-ring sticking compound for mineral lubricating oils.

EXAMPLE VI

Two parts of cracked wax olefins, 1 part salicylic acid and 3 parts lubricating oil were heated at 125° C. for 3 hours in the presence of an excess of boron trifluoride. The product was purified and converted to the calcium salt as described in Example II.

EXAMPLE VII

Two parts cracked wax olefins, 1 part salicylic acid and 3 parts oleyl alcohol were heated under reflux at 125° C., boron trifluoride being continuously introduced. The product was purified and converted to the calcium salt as described in Example II.

EXAMPLE VIII

Forty parts of a mixture of C_8 and C_9 olefins was polymerized at 50° C., using aluminum chloride as catalyst. Subsequently 10 parts phenol was added, and the mixture was heated at 100° C. for 2 hours. The mixture of alkylate and polymerizate was converted to the calcium salt by heating at 90° C. with calcium hydroxide. The product had anti-ring sticking properties when added to mineral oil. A 10% excess of calcium hydroxide was present in the final product.

EXAMPLE IX

Phenol was alkylated with diisobutylene, concentrated sulfuric acid being used as catalyst. Twenty parts of the alkylate phenol was added to 80 parts of a mixture of C_5 to C_{10} olefins, and 10 parts of aluminum chloride. The mixture was heated for three hours at 100° C., after which the product was purified and converted to the zinc salt as described in Example I.

EXAMPLE X

In order to determine the effect of the compounds produced as described above, on the lubricating properties or characteristics of lubricating oils, tests were conducted in which an Edeleanu extracted mineral lubricating oil was subjected, both in the presence and absence of additives, to the so-called "spiral" test, in which a stream of the oil is passed over a metal spiral maintained at an elevated temperature, to determine the amount of residue remaining on the surface of such spiral. The results of the tests are given in Table 2, below.

Table 2

Additive	Weight increase of Spiral, Mg.
None	100
1% Calcium salt, prepared as in Example III (at 100° C.)	10
1% Same+0.4% calcium cetyl phosphate	5
1% Calcium salt prepared as in Example VI	5
1% Calcium salt prepared as in Example VII	15

EXAMPLE XI

Portions of a mineral lubricating oil, both unmodified and containing 1% of the calcium salt prepared as described in Example III, (the mixture alkylate and polymerizate being formed at 100° C.) were employed as lubricants in a gasoline engine. The engine conditions were as follows:

Mean effective pressure	5.2 kg. per sq. cm.
Speed	1200 R. P. M.
Temperature (at cylinder wall) of ethylene glycol cooling medium	195° C.
Temperature (at cylinder head) of cooling medium	85° C.
Temperature of cylinder wall	215° C.±10° C.
Temperature of lubricant in crank-case	70° C.±10° C.

Table 3, below, gives a comparison of the deposits resulting from the use of both unmodified oil, and the same oil containing the calcium salt:

Table 3

Lubricant	No Additive	1% Ca salt
Duration of test, hours	12	16
Portion of 1st Ring which was stuck per cent	65	0
Portion of 2nd Ring which was stuck per cent	0	0
Portion of 3rd Ring which was stuck per cent	85	0
Deposit in ring grooves and lands grams	0.8	0.02
Deposit on side walls of piston do	0.28	0.02
Deposit on inside of piston do	0.9	0.07

EXAMPLE XII

Several Pennsylvania neutral lubricating oils (SAE 30) were tested as lubricants in a Caterpillar Diesel engine. The oils were tested in unmodified form as well as in the presence of additives. The conditions were as follows:

Duration of tests	18 hours
Output	17.7 effective horsepower
Mean effective pressure	5.5 kg. per sq. cm.
Speed	850 R. P. M.
Temperature of cooling water	80° C.
Temperature of lubricant	62–65° C.

Table 4 presents a comparison of deposits formed during the tests made.

Table 4

LUBRICANT #1

Additive	None	1% Ca Salt [1]	1% Ca Salt [1]+ 0.4% Ca Cetyl Phosphate
Deposit in 1st ring groove grams	0.27	0.01	0.01
Deposit on 1st ring do	0.02	0.02	0.01
Deposits on other rings and grooves grams	0.12	0.04	0.00
Deposit inside piston do	0.15	0.08	0 00
Deposit on lands do	0.13	0.08	0.09
Sludge on filter and in filter trough grams	0.16	0.05	0.06
Weight loss of piston rings milligrams	60.00	46.00	39.00

[1] Calcium salt of mixture prepared at 100° C. as described in Example III.

LUBRICANT #2

Additive	None	1% Basic Ca Salt [1]
Deposit in 1st ring groove, grams	0.37	0.00
Deposit on 1st ring, do	0.05	0.00
Deposit on other rings and grooves, do	0.22	0.00
Deposit inside piston, do	0.94	0.00
Deposit on lands, do	0.02	0.00
Sludge on filter and in filter trough, do	0.04	0.00
Weight loss of piston rings, milligrams	104.00	48.00

[1] Basic calcium salt prepared as in Example VIII.

I claim as my invention:

1. A lubricating composition comprising a mineral oil containing dispersed therein from 0.5% to 20% of a polyvalent metal salt of a reaction product obtained by simultaneously polymerizing and alkylating in the presence of a Friedel-Crafts catalyst a hydroxy aromatic monocarboxylic acid and an olefin having at least four carbon atoms at a temperature of between 50° to 200° C., and thereafter reheating said reaction product in an inert liquid medium at a temperature of between 250° and 300° C. for about ½ hour.

2. A lubricating composition comprising a mineral oil containing dispersed therein from 0.5% to 20% of a polyvalent metal salt of a reaction product obtained by simultaneously polymerizing and alkylating in the presence of a Friedel-Crafts catalyst a salicylic acid and an olefin at least four carbon atoms at a temperature of between 50° and 200° C., and thereafter reheating said reaction product in an inert liquid medium at a temperature of between 250° and 300° C. for about ½ hour.

3. A lubricating composition comprising a mineral oil containing dispersed therein from 0.5% to 20% of a polyvalent metal salt of a reaction product obtained by simultaneously polymerizing and alkylating in the presence of a Friedel-Crafts catalyst a salicylic acid and a cracked wax olefin at a temperature of between 50° and 200° C., and thereafter reheating said reaction product in an inert liquid medium at a temperature of between 250° and 300° C. for about ½ hour.

4. A lubricating composition comprising a mineral oil containing dispersed therein from 0.5% to 20% of a calcium salt of a reaction product obtained by simultaneously polymerizing and alkylating in the presence of a Friedel-Crafts catalyst a salicylic acid and a cracked wax olefin at a temperature of between 50° and 200° C., and thereafter reheating said reaction product in an inert liquid medium at a temperature of between 250° and 300° C. for from ¾ to 1½ hours.

5. A lubricating composition comprising a mineral oil containing dispersed therein from 0.5% to 20% of a zinc salt of a reaction product obtained by simultaneously polymerizing and alkylating in the presence of a Friedel-Crafts catalyst a salicylic acid and a cracked wax olefin at a temperature of between 50° and 200° C., and thereafter reheating said reaction product in an inert liquid medium at a temperature of between 250° and 300° C. for about ½ hour.

6. A lubricating oil composition comprising a mineral oil containing dispersed therein from 0.5% to 20% of a basic polyvalent metal salt of a reaction product obtained by simultaneously polymerizing and alkylating in the presence of a Friedel-Crafts catalyst therefor an aromatic monocarboxylic acid and an organic compound having more than four carbon atoms and containing at least one double bond, and reheating said reaction product in an inert medium at a temperature of about 250° C. for about ½ hour.

7. A lubricating composition comprising a mineral oil containing dispersed therein from 0.5% to 20% of a basic calcium salt of a reaction product obtained by simultaneously polymerizing and alkylating in the presence of a Friedel-Crafts catalyst therefor a salicylic acid and a cracked wax olefin at a temperature of between 50° C. and 200° C. and thereafter reheating said reaction product in an inert liquid medium at a temperature of between about 250° and 300° C. for about ½ hour.

8. A lubricating composition comprising a mineral oil containing dispersed therein a minor amount sufficient to inhibit ring sticking of a basic zinc salt of a reaction product obtained by simultaneously polymerizing and alkylating in the presence of a Friedel-Crafts catalyst therefor a salicylic acid and a cracked wax olefin at a temperature of between 50° and 200° C., and thereafter reheating said reaction product in an inert liquid medium at a temperature of between about 250° and 300° C. for about ½ hour.

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Certificate of Correction

Patent No. 2,483,859 **October 4, 1949**

MINTJE VAN LOON

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

Column 9, line 30, after the word "olefin" insert *having* ; column 10, lines 32 and 33, for "a minor amount sufficient to inhibit ring sticking" read *from 0.5% to 20%* ;

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 2nd day of May, A. D. 1950

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

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