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3,385,790

ANTIOXIDANT COMPOSITIONS

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17,634/65

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ABSTRACT OF THE DISCLOSURE

Compositions which exhibit improved lubricating oil qualities and a reduced tendency towards pitting of metal members by the incorporation of an alkenylsuccinic compound-polyamine reaction product, a Group II metal dithiophosphate at a minimum concentration of about 1% and an aralkyl phenol into a lubricating oil. The compositions can be utilized for the lubrication of internal combustion engines.

This invention relates to antioxidant compositions and to the use of antioxidant compositions in lubricating oils.

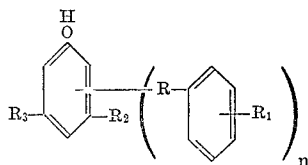
When conventional lubricating oils are subjected to high operating temperatures for prolonged periods of time, they show a tendency to undergo oxidation and decomposition. As well as having a generally adverse effect on the quality and lubricity of the oil, the processes of oxidation and decomposition can give rise to acidic substances that have a corrosive action on metal with which the lubricating oil comes into contact.

A wide variety of materials have been proposed or used as additives in lubricating oils to counteract the effects of the oxidation of the oil, including certain metal derivatives of dithiophosphoric acids, in particular zinc dialkyl dithiophosphates.

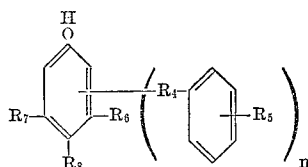
Dithiophosphates of this type are believed to act both as antioxidants by decelerating the normal process by which the oil is oxidized, and as corrosion inhibitors by an interaction with metallic surfaces. However, there is associated with the use of dithiophosphates a tendency for adverse side effects to develop, among which are piston ring sticking and metal pitting. Such side effects become more pronounced as the temperature to which the oil is subjected increases, and are also more pronounced when the dithiophosphate is used in conjunction with certain detergent-type additives.

We have now found that lubricating oil compositions containing metal dithiophosphates singly or in conjunction with detergent-type additives can be stabilized against adverse side effects by incorporating into the lubricating oil compositions a phenolic compound selected from

(a) An aralkyl phenol represented by the structure



(b) An aralkyl 4-alkyl phenol represented by the structure



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and (c) mixtures of (a) and (b); wherein R and R₄ each are selected from the group consisting of alkylene and alkenylene; R₁ and R₅ each are independently selected from the group consisting of hydrogen, alkyl, aryl, substituted alkyl, substituted aryl, halogen, nitro and aralkyl; R₂, R₃, R₆ and R₇ each are selected from the group consisting of hydrogen, alkyl, halogen, nitro, phenyl and substituted phenyl, provided that when any one of R₂, R₃, R₆ and R₇ is hydrogen the group represented by R₁—phenyl—R— and R₅—phenyl—R₄—can occupy that position relative to the phenolic hydroxyl that is occupied by hydrogen; n and m are whole numbers having a value of 1 to 2; and R₈ is alkyl having from 8 to 24 carbon atoms.

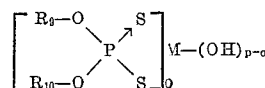
In addition, the present invention relates to antioxidant compositions comprising an oil-soluble metal derivative of a diester of dithiophosphoric acid and a phenolic compound as set out above.

The invention also includes lubricating oil compositions comprising a lubricating oil and a minor proportion of an antioxidant composition of this invention.

The presence of a phenolic compound in a lubricating oil composition as defined above is of particular value where the amount of the dithiophosphate present in the composition is at least 1% of the total weight of the composition and, in addition, where the composition contains an alkenylsuccinic anhydride-amine reaction product as a detergent additive.

The preferred metal derivatives of diesters of dithiophosphoric acids and the preferred phenolic compounds for use according to the present invention are respectively the zinc dialkyl dithiophosphates and the bis(α-methylbenzyl) derivatives of phenol and 4-alkyl-substituted bis(α-methylbenzyl) derivatives of phenol.

The oil-soluble metal derivatives of diesters of dithiophosphoric acid, hereinafter referred to as dithiophosphates, are compounds that are normally represented by the formula:



wherein R₉ and R₁₀ are each selected from the group consisting of alkyl, cycloalkyl, aralkyl, aryl, substituted aryl and substituted alkyl, o is a whole number having a value of 1 to p, p is the valence of M and M represents a metal atom.

The preferred dithiophosphates are those compounds wherein R₉ and R₁₀ are each alkyl radicals containing at least 3 carbon atoms, preferably containing from 3 to 20 carbon atoms, said alkyl radical having either a straight or branched chain. Typical examples of alkyl radicals are isopropyl, isobutyl, n-pentyl, n-hexyl, 4-methylpent-2-yl, 1-methylhexyl, n-octyl, 2-ethylhexyl, n-decyl, n-dodecyl, n-tetradecyl and cetyl.

Typical examples of cycloalkyl radicals wherein either R₉ or R₁₀ or both are cycloalkyl are cyclohexyl and methylcyclohexyl. Typical aralkyl radicals are benzyl and phenyl-substituted alkyl radicals wherein the alkyl radical contains at least 3 carbon atoms. Typical examples of substituted aryl compounds are alkylphenyl wherein the alkyl substituent contains from about 3 to 20 carbon atoms.

With regard to the metal, the derivatives of diesters of dithiophosphoric acid are generally those of metals of Group II of the Mendelyev Periodic Table, for instance, calcium, barium, cadmium and zinc. Zinc, however, is the preferred metal.

In addition to the metal dithiophosphates wherein o is the valence of M, it has also been found that the basic salts of dithiophosphates are also useful and contemplated within the scope of this invention. Thus, when o

is a number less than the valence of M, that is, p , there can be formed a basic salt with a diester of dithiophosphoric acid. A typical example of a basic salt would be a zinc hydroxide dialkyl dithiophosphate.

The oil-soluble metal derivatives of diesters of dithiophosphoric acid are normally prepared by the action of the appropriate alcohol or mixture of alcohols on phosphorus pentasulfide in proportions such that the product is a diester acid, which in turn is neutralized by reaction with an oxide, hydroxide or carbonate of the required metal.

Specific examples of the oil-soluble metal derivatives that are useful according to the present invention are the zinc derivatives of the following dithiophosphoric acids: diisopropyl; diisobutyl; di-sec-amyl; di-n-hexyl; di(1,3-dimethylbutyl); isopropyl, 2-ethylhexyl; isobutyl, 2-ethylhexyl; di(2-ethylhexyl); isopropyl, n-decyl; sec-butyl, cyclohexyl; dicyclohexyl; isopropyl, 3-phenylpropyl; and di(p-1,1,3,3-tetramethylbutylphenyl).

The preferred aralkyl phenols represented by (a) are those in which at least one aralkyl group is present in an ortho position relative to the phenolic hydroxyl group. Thus, the preferred aralkyl phenols are those phenolic compounds wherein n is 2, R_2 and R_3 are hydrogen and the aralkyl group occupies either the 2, 4 or 2, 6 position in relation to the phenolic hydroxyl group.

In general, it is preferred that R and R_4 are alkylene and that the number of carbon atoms in the alkylene group does not exceed four. Typical examples of the groups R_1 -phenyl- R and R_5 -phenyl- R_4 are phenylethyl, tolylethyl and phenylpropyl, phenyl n-alkylene and groups containing a secondary or tertiary carbon linking atom as, for example, α -methylbenzyl, α -ethylbenzyl and α,α -dimethylbenzyl. When n and m have a value of 2, the groups R_1 -phenyl- R and R_5 -phenyl- R_4 can be different with respect to the substituents R_1 and R_5 . Typical example of the two groups represented by R_1 -phenyl- R and R_5 -phenyl- R_4 which are attached to the same phenol nucleus are tolylethyl and xylylethyl.

Although the aralkyl phenol compounds as represented by (a) have been found to inhibit and control the adverse side effects of lubricating oil compositions containing dithiophosphates, it has been found that the aralkyl 4-alkyl phenols represented by (b) are more effective apparently due to the 4-alkyl group. The 4-alkyl group imparts better oil solubility to the phenolic compound and in addition provides greater oil solubility to the phenolic compound as the phenolic compound acts as an inhibitor in lubricating oil compositions. Thus, it has been found that an alkyl group containing at least 8 carbon atoms and up to 24 carbon atoms provide excellent oil solubility and enhanced properties to the aralkyl phenol compounds.

The alkyl group, that is, R_6 , can be arranged in either a straight or branched chain. Examples of such alkyl groups are octyl, nonyl, dodecyl, tridecyl, tetradecyl, pentadecyl and octadecyl groups. In practice, the alkyl group is often one derived from an alkylate fraction, for example, an octyl group corresponding to diisobutylene, a nonyl group corresponding to propylene trimer, or a dodecyl group corresponding to propylene tetramer or triisobutylene. Such alkylate fractions are in some instances isomeric mixtures, and where this is so the alkylated derivative of aralkyl phenols are correspondingly heterogeneous. Such mixtures are, however, fully comparable in performance with the pure aralkyl 4-alkyl phenols while having economic advantages over the latter.

In general, the phenolic compounds represented by (a) and (b) which are preferred are those in which R_2 , R_3 , R_6 and R_7 are hydrogen. However, compounds containing one or more additional hydrocarbon substituents in the 3 or 5 position relative to the phenolic hydroxyl group are also effective and contemplated within the scope of this invention. Such a substituent is normally an alkyl group, for example, a methyl, ethyl, or propyl group,

and a typical example of a compound represented by (a) is 2,4-diaralkyl-m-cresol. In addition, the 3, 5 substituent can be alkenyl, for example, allyl, or an aryl group, for example, phenyl or tolyl. In general, it has been found that the 3, 5 position in relation to the phenolic hydroxyl group is a non-interfering position, that is, there is in general no advantage in having this position occupied by any substituent. It is, therefore, preferred that the 3, 5 position is not occupied by any substituent although such substituent does not adversely affect any of the properties of the phenolic compound as represented by (a) and (b).

Specific examples of phenolic compounds that can be used according to the present invention are 2,4-bis(α -methylbenzyl) phenol, 2,6-bis(α -methylbenzyl) phenol, 2,6-bis(α -methylbenzyl) - 4(1',1',3' - tetramethylbutyl)-phenol, 2,6 - bis(α,α -dimethylbenzyl)-4(1',1',3',3'-tetramethylbutyl) phenol, 2,6-bis(α -methylbenzyl)-4(4',4'-dimethylhept-2'-yl) phenol and 2,6-bis(α -methylbenzyl)-4-dodecylphenol. The dodecyl group in the last-named phenolic compound can be conveniently derived from propylene tetramer.

In the lubricating oil compositions of this invention, the base oil is normally a hydrocarbon oil, and can be in addition dicarboxylic acid esters such as 2-ethylhexyl sebacate, alkylated benzene, alkylene oxide polymers, silicate esters, silicone polymers and the like or mixtures thereof.

Usually the hydrocarbon oil is of mineral origin, although it can be synthetic, for instance a polyolefin. The oil base may also contain an oil of animal or vegetable origin, for example, lard oil or castor oil.

While the presence of the phenolic compounds as represented by (a) and (b) in a lubricating oil composition of this invention is particularly adapted to deal with problems that arise where the metal derivative of the dithiophosphoric acid is present in lubricating oils at a level of about 1% by weight, beneficial effects are also apparent where the dithiophosphate forms a smaller proportion of the total composition. Generally the dithiophosphate will be present in an amount of from about 0.10 to about 10% by weight of the total composition.

The phenolic compound of this invention is normally present in lubricating oil compositions in an amount varying from about 0.05 to about 10% of the total weight of the composition, preferably from about 0.05 to about 4%.

The concentrates and antioxidant compositions of the invention are, of course, intended for addition to lubricating oils, and the relative proportions of the antioxidants in these mixtures are therefore selected according to the proportions required in the lubricating oil composition.

The proportion of oil in the concentrates of the invention can vary from, for example, 20% to 80% of the total weight of the concentrate.

The antioxidant compositions, concentrates and lubricating oil compositions of the present invention can optionally contain other additives having beneficial effects on the properties of the oil. Such additives include for instance materials having detergent properties, for example, oil-soluble alkaline earth metal derivatives of phosphosulfurized polyolefins, alkali or alkaline earth metal salts or petroleum of alkylbenzene sulfonates or ashless detergents, for instance alkenyl-succinic anhydride-amine reaction products, anti-wear additives, for example, aryl phosphates such as for instance tricresyl phosphate, viscosity improvers and pour-point depressants.

The alkenylsuccinic anhydride-amine reaction products referred to above are usually derived from alkenylsuccinic anhydrides wherein the alkenyl group contains a relatively large number of carbon atoms. These anhydrides are generally made by the direct action of a polyolefin on maleic anhydride, suitable polyolefins being low polymers of C_2 to C_5 olefins, for instance, polypropylenes, polybutylenes or polyisobutylenes. The alkenyl group contains

generally from 50 to 200 carbon atoms. The amines with which the alkenylsuccinic anhydrides are reacted are in most instances aliphatic polyamines, especially polyalkylene-polyamines such as for instance diethylenetriamine and tetraethylenepentamine. Also belonging to the class of ashless detergents or dispersants for lubricating oils are alkenylsuccinic anhydride-amine reaction products modified by the use of a third component, for example, as described in United States Patent 2,568,876.

Ashless detergents of the above type may be used in lubricating oils at a range of concentrations, being present in amounts of, for example, from about 0.1 to 5% of the total weight of the composition. When there is also present a metal dithio phosphate, the advantages to be gained by also including a phenolic compound in the lubricating oil composition becomes particularly apparent where the amount of the alkenylsuccinic anhydride-amine reaction product is about 1.25% or more of the total weight of the composition.

The invention is illustrated by the following non-limiting examples.

EXAMPLE 1

This example describes the production of an antioxidant composition and lubricating oil composition according to the invention, and illustrates the improved performance of such an oil composition in comparison with a similar lubricating oil not containing a phenolic compound.

An antioxidant composition was prepared by mixing a zinc isopropyl 2-ethylhexyl dithiophosphate with bis(α -methylbenzyl) phenol containing the 2,4-isomer as the major component, in the proportions by weight of 5 parts to 1 part.

A lubricating oil formulation (A) having the following composition was then prepared:

Formulation A:	Parts by weight
Mixed detergent containing barium and calcium sulfonates and an alkenylsuccinic anhydride-polyalkylenepolyamine reaction product	4.75
Antioxidant composition	1.5
Mineral oil of viscosity 11 centistokes at 210° F.	93.75

and for comparison, a formulation (B) having the following composition, i.e., one containing the same amount of the zinc dialkyldithiophosphate as Formulation A:

Formulation B:	Parts by weight
Mixed detergent as in Formulation A	4.75
Zinc isopropyl 2-ethylhexyl dithiophosphate	1.25
Mineral oil of viscosity 11 centistokes at 210° F.	94.0

In one comparison of the two formulations, each was used in turn as the lubricant in a 4-cylinder gasoline engine. In each test, the engine was run at normal operating temperature (275° C. in the ring belt area), and the pistons (each of which carried two piston rings) and cylinders were examined after continuous operation for 100 hours.

The following observations were recorded.

TABLE I

Formulation	No. 1 Piston	No. 2 Piston	No. 3 Piston	No. 4 Piston
A-----	All Rings Free			
B-----	Both rings free.	Top ring tight. Bottom ring free.	Top ring tight. Bottom ring free.	Top ring stuck. Bottom ring stuck.

The beneficial effect of the aralkyl phenol in reducing the amount of deposit formation in the piston ring belt area is apparent.

In a further test, Formulations A and B were compared as lubricants in the Petter W. 1 gasoline engine test run under I.P. 176/65 conditions. The temperature in the undercrown region during operation of the engine was 255° C. The performance of the lubricating oil was assessed by piston undercrown and skirt ratings, the said ratings being determined by visual inspection, and being represented by a figure on a scale from 0 to 10 where 0 corresponds to extremely dirty and 10 to perfectly clean.

A third comparison was made between the increases in the viscosities of the oil formulations that occurred during the period of the Petter engine test.

From the results given in the following table the formulation containing the aralkyl phenol is again shown to be superior.

TABLE II

	Formulation A	Formulation B
Piston skirt rating.....	10.0	9.4
Piston undercrown rating.....	9.6	9.1
Percent increase in viscosity of formulation.....	20.7	26.9

EXAMPLE 2

This example describes the production of a lubricating oil composition according to the invention and compares its effect on the wear of chilled tappets with that of other formulations not containing an aralkyl phenol.

The components in the composition (Formulation C) according to the invention were as follows:

	Parts by weight
Mixed detergent as in Formulation A (Ex. 1)	4.75
Zinc isopropyl 2-ethylhexyl dithiophosphate	1.0
Bis(α -methylbenzyl) phenol	0.25
Mineral oil of lubricating viscosity	94.0

A formulation was prepared in which the amounts of detergent and dithiophosphate additives were the same as in Formulation C but the bis(α -methylbenzyl) phenol was omitted, the proportion of mineral oil being increased correspondingly (Formulation D).

The results obtained in an examination under standard conditions of the effects of the various formulations on chilled tappets are given below.

TABLE III

Formulation:	Corrosive wear
C-----	Less than 10% pitting.
D-----	Very badly pitted.

Comparison of the behavior of Formulations C and D shows that this adverse effect is substantially reduced by including phenolic compounds in the formulation.

EXAMPLE 3

An antioxidant composition was prepared by mixing a zinc isopropyl 2-ethylhexyl dithiophosphate and a 2,6-bis(α -methylbenzyl)-4-nonyl phenol in the proportions by weight of 5 parts to 1 part. This mixture was used in producing a lubricating oil formulation having the following composition:

	Parts by weight
Mixed detergent as in Formulation A (Ex. 1)	4.75

Antioxidant composition	1.5
Mineral oil of viscosity 12.7 centistokes at 210° F.	93.75

TABLE IV.—100 HOURS TEST DURATION

Formulation	No. 1 Piston	No. 2 Piston	No. 3 Piston	No. 4 Piston
Example 3-----	All Rings Free			
B-----	Both rings free.	Top ring tight. Bottom ring free.	Top ring tight. Bottom ring free.	Top ring stuck. Bottom ring stuck.

The formulation as represented by Example 3 was continued for an additional 100 hours and at the termination of the 200 hour test period it was found that all of the piston rings were free. Formulation B could not be continued for an additional 100 hours due to the overall condition of the rings that existed at the end of 100 hours.

As is demonstrated by Table I, Table II, Table III and Table IV, the incorporation of the phenolic compound inhibits and controls the adverse side effects which are present in lubricating oil formulations containing a dithiophosphate singly or in combination with an ashless detergent. The performance of the dithiophosphate with respect to pitting and ring sticking is greatly improved when a phenolic compound is incorporated into the dithiophosphate compositions. The phenolic compounds by themselves do not provide the overall qualities as provided by the metal dithiophosphates. Thus, the combination of the two additives, that is, dithiophosphates and a phenolic compound, provides lubricating oil formulations which have enhanced properties with respect to the lubricating qualities that are needed in lubrication of moving parts. As is noted from these results, the ratings of the various piston rings showed that all rings were free at the end of the 100 hour duration. This is of significance in that the rings provide the seal between the piston and cylinder wall which is necessary in order to maintain compression within the cylinder. In addition, the rings prevent oil which is on the cylinder walls from reaching the combustion cylinder. Lubricating oil formulations in general have been found to require the dithiophosphates and ashless detergents to enhance and provide other properties of a lubricating oil formulation. It is of particular importance with respect to this invention that the presence of phenolic compounds in no way detracts from the overall properties which are provided by a dithiophosphate and ashless detergent compositions.

As is noted from Table IV the test duration was continued for an additional 100 hours which significantly demonstrates the increased effectiveness of the aralkyl 4-alkyl phenol compounds in inhibiting and controlling the adverse side effects of the dithiophosphates. The presence of the oil-solubilizing 4-alkyl group provides superior performance in compositions comprising a zinc dithiophosphate singly or in combination with an ashless detergent. This is of particular importance since it provides lubricating oil compositions which continue to provide efficient lubrication over extended periods of time.

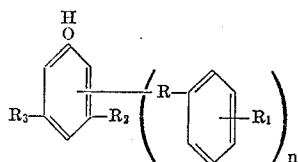
While this invention has been described with respect to various specific examples and embodiments, it is understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

What is claimed is:

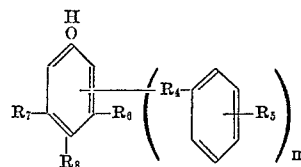
1. A composition comprising a major amount of a lubricating oil and

(A) from about 0.05 to about 10% by weight of a phenolic compound selected from the group consisting of

(1) an aralkyl phenyl represented by the structure



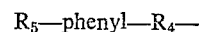
(2) an aralkyl 4-alkyl phenol represented by the structure



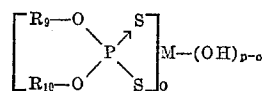
and

(3) mixtures of (1) and (2)

wherein R and R₄ each are selected from the group consisting of alkylene and alkenylene having from about 1 to about 4 carbon atoms; R₁ and R₅ are each selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, alkaryl, halogen and nitro; R₂, R₃, R₆ and R₇ are each selected from the group consisting of hydrogen, alkyl, alkenyl, halogen, nitro, aryl, alkaryl and aralkyl, provided that when any one of R₂, R₃, R₆ and R₇ is hydrogen the group represented by R₁-phenyl-R— and

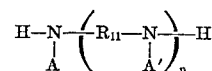


can occupy that position relative to the phenolic hydroxyl that is occupied by hydrogen; n and m are each whole numbers having a value of from 1 to 2; and R₈ is alkyl having from 8 to 24 carbon atoms; (B) from about 1 to about 10% by weight of a metal derivative of dithiophosphoric acid represented by the structure



wherein R₉ and R₁₀ are each selected from the group consisting of alkyl having from 3 to 20 carbon atoms, cycloalkyl, aryl, aralkyl and alkaryl wherein the said alkyl portion of the aralkyl and alkaryl groups has from 1 to 20 carbon atoms; o is a whole number having a value of 1 to p; p is the valence of M and M represents a Group II metal atom; and

(C) from about 0.1 to about 5% by weight of a product prepared by the reaction of an alkenylsuccinic compound having from 50 to 200 carbon atoms in the alkenyl portion and a polyamine conforming for the most part to the structure



wherein n is an integer having a value of from 1 to 10, A and A' each are selected from the group consisting of hydrocarbyl and hydrogen and A and A' can together form the remainder of a heterocyclic ring; and R₁₁ is alkylene containing from 1 to 8 carbon atoms.

2. A composition of claim 1 wherein R₂, R₃, R₆ and R₇ are hydrogen; R₁ and R₅ are selected from hydrogen and alkyl of from 1 to 3 carbon atoms; R and R₄ are alkylene having from 1 to 3 carbon atoms; R₉ and R₁₀ are selected from alkyl having from 3 to 10 carbon atoms and cycloalkyl, A and A' are hydrogen and n is an integer having a value of from 1 to 6.

3. A composition of claim 2 wherein R₈ is alkyl having from 8 to 16 carbon atoms and R₁ and R₅ are hydrogen.

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4. A composition of claim 3 wherein n is an integer having a value of from 2 to 6 and R_{11} is alkylene containing from 1 to 3 carbon atoms.

5. A composition of claim 4 wherein R_{11} is alkylene containing 2 carbon atoms.

6. A composition of claim 4 wherein M is zinc.

7. A composition of claim 5 wherein R_8 is nonyl and M is zinc.

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DANIEL E. WYMAN, *Primary Examiner.*

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,385,790 Dated May 28, 1968

Inventor(s) Henry M. Davies and Arthur S. Thomas

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 5, "Company, a corporation of Delaware" should read -- Chemicals Limited, London, England, a British company --.

SIGNED AND
SEALED

OCT 21 1969

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents