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IMPROVED MINERAL OIL COMPOSITION

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12 Claims. (Cl. 87—9)

This invention has to do in a general way with mineral oil compositions and is more particularly related to mineral oil fractions of the viscous type, such as find use as lubricants and dielectrics, which have been improved in one or more of their properties by the admixture therewith, in minor proportion, of a novel improving agent.

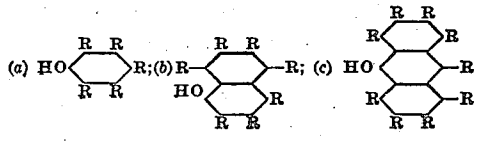
It is well known to those familiar with the art, that mineral oil fractions, such, for example, as those derived from paraffin base crudes which have been refined for use as lubricants, normally contain an amount of wax such that the oils congeal or reach a state in which they will not flow at temperatures only slightly below normal temperatures. Such oils are obviously impractical for general use, and while it is possible to remove sufficient of the wax by further refining operations so as to materially reduce the "pour point" of the oil, such wax removal is not only expensive but it also reduces the lubricant quality of the oil. It has therefore become the practice to incorporate in such oil fractions a compound or composition which possesses the property, in minor proportion, of modifying or retarding wax crystallization so that impairment of flow does not take place except at temperatures well below those normally encountered in the use of the oil. Addition agents which function in the manner just described are generally referred to in the art as "pour depressants".

It is also well known to those familiar with the art that mineral oil fractions obtained by the usual methods of refining are usually susceptible to oxidation particularly where the conditions of use subject them to elevated temperatures, contact with air, exposure to light, etc. Oxidation of the oil fraction is highly undesirable, the deleterious effect manifesting itself in various ways depending upon prior refining operations and the environment in which the oil is used. A motor lubricant, for example, under the oxidizing conditions encountered in the crank case tends to develop sludge and carbonaceous deposits which accumulate about the piston rings, filling the slots in the oil rings and causing the rings to stick in their grooves to a greater or less extent. Also where certain types of alloy bearings (such as cadmium silver bearings) are being used in the presence of the lubricant, especially one obtained by a solvent extraction process, oxidation of the oil manifests itself in corrosion of the bearing metal. Moderately refined oils such as those used for turbine oils normally yield acid and sludge on oxidation and highly refined oils, which are also used in turbines and transformers develop acidity. To stabilize the oil fractions against these effects of oxidation various additive agents, known as "oxidation inhibitors" have been developed.

It is the primary object of this invention to provide a mineral oil composition containing a novel improving agent which possesses the dual function of a pour point depressant and an oxidation inhibitor. Our invention is predicated upon the discovery that such a compound or product can be obtained by reacting a wax substituted hydroxyaromatic compound with an organic phosphorus and chlorinic compound identified in the literature as "ortho phosphitobendoyl chloride" or "(2-chloroformyl phenyl)—meta phosphite". This reaction, details of which will be hereinafter discussed in greater detail, is attended with the evolution of HCl, and the reaction product is a complex compound or mixture of closely related complex compounds characterized by the presence of a wax substituted aryl nucleus, phosphorus and oxygen.

The first reactant referred to above as a wax substituted hydroxyaromatic compound can be obtained by the condensation in the presence of a Friedel-Crafts catalyst of a halogenated heavy aliphatic hydrocarbon (characterized by long chains having at least twenty carbon atoms) with a hydroxyaromatic compound (mono or polycyclic, mono or poly hydric and substituted or unsubstituted). Preferably the halogenated aliphatic hydrocarbon is a chlorinated high molecular weight aliphatic material of the type characteristic of the heavier products of petroleum, special preference being given to a petroleum wax as a source of the chlorinated material.

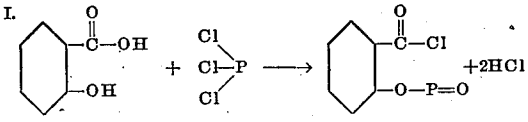
The hydroxyaromatic compounds which are condensed with the aliphatic material in the Friedel-Crafts reaction to obtain the first reactant mentioned above are represented, for the most part, by the following formulae:



wherein the R's are radicals chosen from the group consisting of hydrogen, hydroxy, alkyl, aryl, aralkyl, alkaryl, aroxy and alkoxy radicals. In general it is preferred to use those compounds wherein the R's are selected from the group consisting of hydrogen and hydroxy, and within this group preference is had for compounds of the single ring type (*a*), the preferred specific rompound being phenol (mono hydroxy benzene). Other compounds which may be found useful in preparing the "first reactant" are benzyl phenol, resorcinol, o-hydroxydiphenyl, beta-naphthol, p-cresol, hydroquinone, methyl naphthol, benzyl naphthol, anthranol and the like.

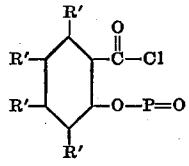
The second reactant used in producing our novel oil improving agent, which has been generally referred to herein as "ortho-phosphitobenzoyl chloride" is obtained by reacting phosphorus trichloride with ortho hydroxy benzoic acid (salicyclic acid) or alkyl substituted, aryl substituted, or aralkyl substituted—ortho hydroxy benzoic acid in substantially equi-molar proportions. This reaction is carried out preferably at a temperature slightly above atmospheric until the evolution of hydrochloric acid has substantially ceased and may be illustrated (using unsubstituted salicyclic acid) by the following equation:

I.



The class or group of compounds contemplated herein as the second reactant, taking into consideration the alternative of using a substituted salicyclic acid in the reaction of equation I may be represented by the following general formula:

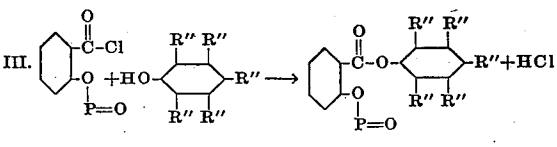
II.



in which R' represents hydrogen, alkyl, aryl or aralkyl.

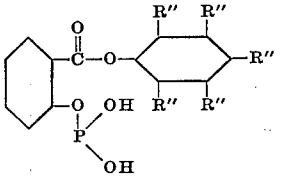
In obtaining the final oil-improving agents from the two reactants described above, the wax-hydroxyaromatic compound and the "ortho-phosphitobenzoyl chloride" compound are reacted together in substantially equimolar proportions at elevated temperature until the evolution of hydrochloric acid has substantially ceased after which the reaction mixture is washed to obtain the final product. This reaction may be illustrated by the following equation:

III.



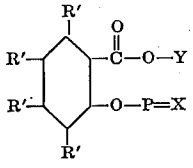
in which at least one of the R''s represents a heavy alkyl radical corresponding to those which characterize petroleum wax, the remaining R''s being selected from the group consisting of hydrogen, hydroxyl, aryl, alkyl, aralkyl, aroxy, and alkoxy radicals. It is possible that two OH groups have hydrated the phosphorus atom in the water-washing step, in which event the formula of the product of equation III becomes:

IV.

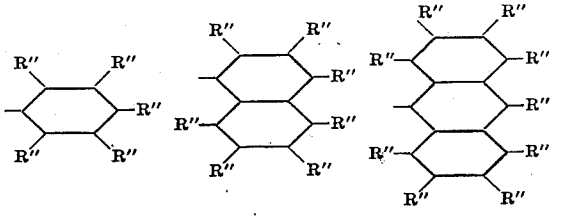


It is to be understood that a general formula for a series of reactants and reaction products of the type discussed above involves a degree of uncertainty and we therefore do not wish to be bound by any theory as to the molecular composition or exact chemical name of the product or products contemplated herein. However, for purpose of illustration, reaction products of the general type described above as oil improving agents may be represented by the following general formula

V.



wherein R' has the same significance defined above; X represents an oxygen atom or two OH radicals attached to P and Y represents a radical selected from the group represented by the following formulae:



wherein R'' has the same significance defined above. In addition to this illustrative formula we have arbitrarily designated products of this general type by the name of "wax aryl ortho-phosphitobenzoates".

The details in the procedure which may be conveniently followed in synthesizing oil improving agents of the type contemplated herein, together with further details as to the physical properties and behaviour of these products in mineral oil, will be best appreciated from the following examples:

PREPARATION OF "WAX-PHENYL ORTHO-PHOSPHITO-BENZOATE"

A. Wax phenol (first reactant)

A crystalline petroleum wax having a melting point of about 130° F. was chlorinated by heating the wax to about 200° F. and bubbling chlorine gas through the molten wax until it had combined with or permanently absorbed about 14% chlorine, the wax-chlorine composition corresponding substantially to a mono or a mixture of mono- and di-chlorwax. The wax substituted phenol was formed by mixing the chlorwax and phenol together in suitable proportions, heating to a temperature from about 120° F. to about 150° F. and then adding a Friedel-Crafts catalyst

(aluminum chloride) in an amount corresponding to from 2% to 10% of the weight of the chlorwax. The temperature is then slowly raised to about 250°–350° F. until completion of the reaction is indicated by substantial cessation of HCl evolution.

This product may be water washed to remove the aluminum chloride, but we consider it preferable to use the wax-phenol-aluminum chloride complex as one of the reactants to be used in obtaining our final product.

The degree of wax substitution in the final product may be varied by varying the proportions of phenol (hydroxyaromatic) and chlorwax (halogenated high molecular weight aliphatic compound) used in the above reaction. The particular product derived from chlorwax and phenol, which our tests indicate as being preferable, is obtained by using an amount of chlorwax (14% chlorine content) containing two atomic proportions of chlorine and one molecular proportion of phenol. This product is arbitrarily termed a "di-wax" phenol. "Tri"- and "tetra"-wax phenols can be obtained by using ratios of one molecular proportion of phenol to a quantity of chlorwax containing three and four atomic proportions of chlorine respectively.

B. Ortho-phosphitobenzoyl chloride (second reactant)

One mole of phosphorus trichloride and one mole of salicylic acid were mixed together in a reaction vessel and the mixture heated gently on the water bath to about 158° F. at which temperature there was a moderate evolution of hydrogen chloride. When this evolution had begun to subside the temperature was raised to about 194° F. to insure completion of the reaction as indicated by substantial cessation of HCl evolution. The product of this reaction, represented by Equation I above, according to the system of nomenclature used by the Chemical Society (London) is termed ortho-phosphitobenzoyl chloride.

C. Final product ("wax-phenyl ortho-phosphitobenzoate")

488 grams (0.5 mol) of the tetra-wax phenol-aluminum chloride complex of step A above was melted by heating to about 122° F. in a reaction vessel and 101 grams (0.5 mol) of ortho-phosphitobenzoyl chloride was added thereto at one time. The temperature of the reaction mixture was raised, by the application of external heat, from 122° F. to about 302° F. over a period of about 1½ hours. During this time there was a brisk evolution of hydrogen chloride, and the temperature was held in the neighborhood of 300° F. for another hour to assure completion of the reaction.

A "di-wax" product was also prepared following the same general procedure using a di-wax phenol-aluminum chloride complex instead of the tetra-wax phenol complex.

After this reaction was complete the product was washed with hot water to remove aluminum chloride. It is advantageous in this washing operation to add about two percent of an alcohol, such as amyl alcohol, to the wash water, to decrease the tendency toward emulsification. The product was washed three times with equal volumes of water containing two percent of amyl alcohol after which it was dissolved in benzene and the benzene solution was further washed three times with water-amyl alcohol solution. The benzene was removed by distillation to give the final product which we have termed for purpose of identification, a di-, tri- or tetra-wax-phenyl, ortho-phosphitobenzoate, depending on the extent to which the wax-phenol has been substituted with wax. Broadly, these products may be termed wax-phenyl ortho-phosphitobenzoate.

IMPROVEMENT OF MINERAL FRACTIONS EFFECTED BY WAX-ARYL ORTHO-PHOSPHITOBENZOATE

A. Stabilized motor oils

To illustrate the inhibiting action of the improving agents contemplated herein upon mineral oil fractions of the type used as motor lubricants, the following test was conducted with a solvent refined motor oil, S. A. E. 20, having a Saybolt viscosity of 55.3 sec.; at 210° F. and a flash point of 435° F.

This test comprised passing a current of air, at the rate of 2000 ml. per hour, through a 30 gram sample of the oil and the oil blend heated at 347° F. for 22 hours in the presence of a weighed sample of cadmium-silver alloy bearing. The table (I) below shows the loss in weight in milligrams of the test specimen in the mineral oil alone, and in the same oil inhibited with various amounts of the reaction products of "di-wax" and "tetra-wax" phenols with ortho-phosphitobenzoyl chloride, such reaction products being arbitrarily termed "di-wax phenyl ortho-phosphitobenzoate" and "tetra-wax phenyl ortho-phosphitobenzoate" respectively.

Table I

Improving agent	Percent added	Mgs. loss in weight of bearing specimen	
		Oil alone	Inhibited oil
Di-wax phenyl ortho-phosphitobenzoate	0.25	56	0.7
	0.10	56	11.4
Tetra-wax phenyl ortho-phosphitobenzoate	0.25	52	1.0
	0.10	69	48.0

B. Motor oils with depressed pour point

The following data illustrates the pour point depressing action of products of the type contemplated by this invention upon mineral oils of the motor lubricant type. The oil used in these tests was a refined wax containing petroleum lubricant oil having a Saybolt Universal viscosity of 249 sec. at 130° F. and having an A. S. T. M. pour test of +20° F. from the data in Table II below, it will be observed that products of the type contemplated herein are effective, in amounts ranging from 0.125% to 0.5% to reduce the pour point of the oil in amounts ranging from 25° to 50° F.

Table II

Improving agent	Percent in blend	Pour point
		°F.
Di-wax phenyl ortho-phosphitobenzoate	0.50	−30
	0.25	−20
	0.125	−5
Tetra-wax phenyl ortho-phosphitobenzoate	0.50	Below −20
	0.25	Below −20
	0.175	−15

From the foregoing series of tests A and B, it will be seen that the improving agents contem-

plated by this invention possess the property of simultaneously inhibiting an oil against the deleterious effect of oxidation and, at the same time, will depress the pour point of the oil.

C. Stabilized moderately refined oils

Moderately refined oils, such as turbine oils, develop acid and sludge on oxidation. The inhibiting action of the improving agents contemplated herein was demonstrated with a turbine oil of 150 sec. Say. Univ. viscosity at 100° F. and flash point of 400° F. The test involved heating the oil for a period of three days at 230° F. in the presence of copper and with exposure to air. The stabilizing action is illustrated in the table below by the color and acidity or neutralization number (N. N.) of the oil alone and the oil blend before and after aging.

Table III

	Before aging Lovibond color	After aging	
		Lovibond color	N. N.
Turbine oil alone	0.10	15	0.07
Same oil plus 0.10 percent di-wax phenyl ortho-phosphito benzoate	0.10	5	0.03

D. Stabilized highly refined oils

A highly refined oil such as a transformer oil tends to develop acidity on oxidation. The inhibiting effect of the improving agents contemplated herein was determined by heating the oil sample in a glass container for 70 hours at 250° F. in the presence of oxygen. At the end of this period the acid value or neutralization number (N. N.) of the oil was determined, such test being known as the modified German Tar Test. The oil used was a neutral transformer oil having a Saybolt viscosity of 70 seconds at 100° F. and a flash point of 310° F. The results are indicated in Table IV below:

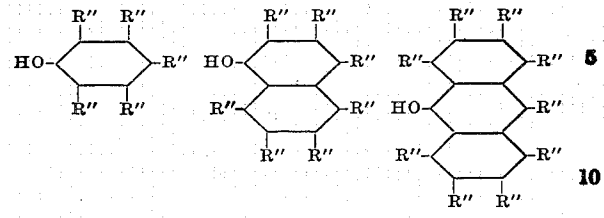
Table IV

Oil sample	N. N. after aging
Oil alone	25
Oil plus 0.10 percent tetra-wax phenyl ortho-phosphito-benzoate	15
Oil plus 0.10 percent di-wax phenyl ortho-phosphito-benzoate	0.03

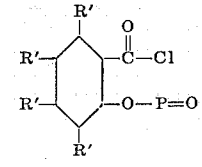
It is to be understood that while we have herein described certain preferred procedures for synthesizing the improving agents contemplated herein, and have designated certain illustrative reactants which may be employed, the invention is not confined to the specific procedures or reactants described above but includes within its scope whatever changes or modifications fairly come within the spirit of the appended claims. In this regard it is particularly pointed out that while we have illustrated the phenolic compounds with structural formulae and have shown polycyclic compounds with the OH group in a fixed location in such formulae, we do not bind ourselves to the specific formulae used but intend to include thereunder such isomers, etc., as will be apparent to those skilled in the art.

We claim:

1. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the product obtained by reacting a compound selected from the group having the general formulae:

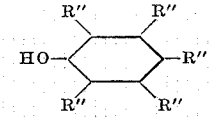


in which at least one of the R''s represents a high molecular weight aliphatic hydrocarbon radical, the remaining R''s being selected from the group consisting of hydrogen, hydroxyl, aryl, alkyl, aralkyl, aroxy, and alkoxy radicals, with a compound having the general formula:

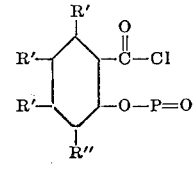


in which the R's are selected from the group consisting of hydrogen, alkyl, aryl and alkaryl radicals, the final product of said reaction possessing the property of depressing the pour point and inhibiting oxidation of the oil.

2. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the product obtained by reacting a compound selected from the group having the general formulae:

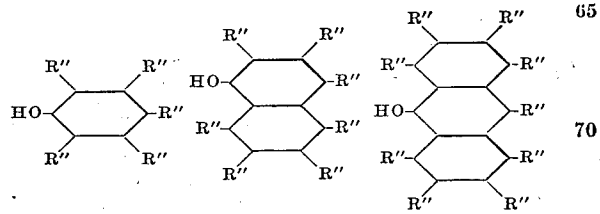


in which at least one of the R''s represents a high molecular weight aliphatic hydrocarbon radical, the remaining R''s being selected from the group consisting of hydrogen, hydroxyl, aryl, alkyl, aralkyl, aroxy, and alkoxy radicals, with a compound having the general formula:



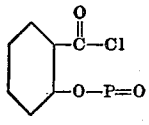
in which the R's are selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals, the final product of said reaction possessing the property of depressing the pour point and inhibiting oxidation of the oil.

3. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the product obtained by reacting a compound selected from the group having the general formulae:



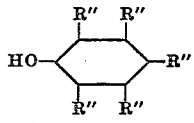
in which at least one of the R''s represents a

high molecular weight aliphatic hydrocarbon radical, the remaining R''s being selected from the group consisting of hydrogen, hydroxyl, aryl, alkyl, aralkyl, aroxy, and alkoxy radicals, with a compound having the general formula:

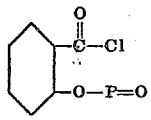


the final product of said reaction possessing the property of depressing the pour point of the oil and stabilizing same against the deleterious effects of oxidation.

4. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the product obtained by reacting a compound selected from the group having the general formulae:



in which at least one of the R''s represents a high molecular weight aliphatic hydrocarbon radical, the remaining R''s being selected from the group consisting of hydrogen, hydroxyl, aryl, aralkyl, aroxy and alkoxy radicals, with a compound having the general formula:



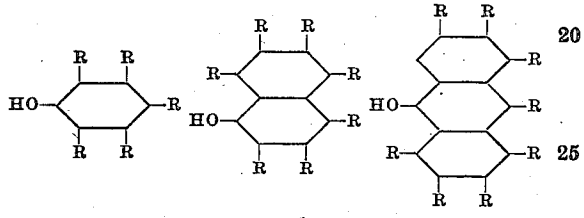
the final product of said reaction possessing the property of depressing the pour point of the oil and stabilizing same against the deleterious effects of oxidation.

5. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the product obtained by reacting the Friedel-Crafts condensation product of a halogenated wax and a hydroxyaromatic compound with the reaction product of phosphorous trichloride and ortho hydroxy benzoic acid.

6. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the final product obtained by: reacting phosphorus trichloride with ortho hydroxy benzoic acid in about equi-molar proportions until the evolution of hydrochloric acid has substantially ceased to obtain one reactant; condensing a hydroxyaromatic hydrocarbon with a halogenated wax in the presence of a Friedel-Crafts catalyst to obtain the other reactant; and reacting the two reactants at elevated temperature until the evolution of hydrochloric acid has substantially ceased, thereafter washing the reaction mixture to obtain the final product which has the property of depressing the pour point of the oil and stabilizing same against the deleterious effects of oxidation.

7. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the final product obtained by: a reacting phosphorus trichloride with ortho hydroxy benzoic acid in about equimolar proportions until the evolution of hydrochloric acid has substantially ceased to obtain one reactant; condensing phenol and chlorinated wax in the presence of aluminum chloride at elevated temperature until the evolution of hydrochloric acid has substantially ceased to obtain the other reactant; and reacting the two reactants at elevated temperature until the evolution of hydrochloric acid has substantially ceased to obtain the final product which has the property of depressing the pour point of the oil and stabilizing same against the deleterious effect of oxidation.

8. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the final product obtained by: reacting phosphorus trichloride with ortho hydroxy benzoic acid in substantially equimolar proportions until the evolution of hydrochloric acid has substantially ceased to obtain one reactant; condensing a member selected from the group consisting of compounds of the general type



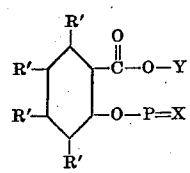
in which R represents radicals selected from the group consisting of hydrogen, hydroxy, alkyl, aryl, aralkyl, aroxy and alkoxy, with chlorinated wax in the presence of aluminum chloride to obtain the other reactant; reacting the two reactants at elevated temperature until the evolution of hydrochloric acid has substantially ceased; and washing the last mentioned reaction mixture to obtain the final product which has the property of depressing the pour point of said oil and stabilizing same against the deleterious effects of oxidation.

9. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the product obtained by reacting a wax substituted hydroxy-aromatic compound with o-phosphitobenzoyl chloride until the evolution of hydrochloric acid has substantially ceased.

10. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the product obtained by reacting tetra-wax phenol with o-phosphitobenzoyl chloride at elevated temperature until the evolution of hydrochloric acid has substantially ceased.

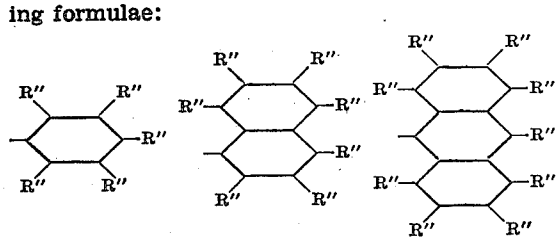
11. An improved mineral oil composition comprising a mineral oil and in admixture therewith a minor proportion of the product obtained by reacting di-wax phenol with o-phosphitobenzoyl chloride at elevated temperature until the evolution of hydrochloric acid has substantially ceased.

12. An improved mineral oil composition comprising a mineral oil fraction and in admixture therewith a compound having the general formula:



in which: the R's represents hydrogen, alkyl, aryl, or alkaryl groups; X represents a single oxygen atom, or two hydroxyl atoms attached to P by separate valences; and Y represents a radical se-

lected from the group represented by the following formulae:



in which at least two of the R''s represent heavy alkyl radicals corresponding to those which characterize petroleum wax, the remaining R''s being selected from the group consisting of hydrogen, hydroxyl, aryl, alkyl, aralkyl, aroxy and alkoxy radicals.

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CERTIFICATE OF CORRECTION.

Patent No. 2,177,923. October 31, 1939.

HENRY G. BERGER, ET AL.

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 18, for "phosphitobendoyl" read phosphitobenzoyl; page 2, first column, line 8-9, for "rompound" read compound; page 3, second column, line 56, for "from" read From; page 4, second column, line 54, claim 2, in the lowermost portion of the formula, for "R''" read R'; 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 2nd day of January, A. D. 1940.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)