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WAX PHENOL-PHOSPHORUS PENTOXIDE REACTION PRODUCTS AND PETROLEUM OIL FRACTIONS CONTAINING THE SAME

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This invention relates to a novel class of chemical compounds prepared by the reaction of wax-substituted hydroxy aromatic compounds with phosphorus pentoxide. More particularly, the invention is concerned with the use of these compounds as additives for petroleum oil fractions to improve the properties thereof.

The use of chemical additives in petroleum oil fractions, such as lubricating oils, fuel oils, gasolines, etc., to improve the properties thereof is well known. Thus, in lubricating oil, additives have been used for the purpose of improving the ability of the oil to resist oxidation in use, for improving the detergent action of the oil, for lowering the pour point, for increasing the viscosity index, for raising the load-carrying capacity of the oil, etc. Additives have also been used in diesel fuels for various purposes, such as to improve ignition quality or to lower the starting temperatures thereof. They have also been used in gasolines for numerous purposes, such as to improve octane ratings and to prevent gum formation and to inhibit the formation of rust on metallic surfaces in contact with the gasoline in pipelines and in storage.

We have now found that the products herein contemplated, i. e. the products obtained by reacting a wax-alkylated hydroxy aromatic compound, such as wax phenol, with phosphorus pentoxide, are capable of providing certain beneficial properties, when used as additives, in petroleum oil fractions, particularly in mineral lubricating oils and gasolines.

In particular, we have found that these compounds are capable of greatly increasing the load-carrying capacities, as well as markedly lowering the pour points, of petroleum lubricating oils. Also, they are very effective as rust inhibitors in gasolines. Accordingly, it is the object of this invention to provide petroleum oil fractions of improved characteristics, said fractions containing minor proportions of the products herein contemplated.

It is a further object to provide petroleum lubricating oils containing these products which oils have relatively high load-carrying capacities and relatively low pour points. It is also an object to provide gasolines containing these products which are strongly resistant to the formation of rust on metal surfaces in contact therewith.

It is realized that products of a somewhat similar character to those contemplated herein have been used heretofore as additives in mineral lubricating oils. Specifically, products prepared by the reaction of phosphorus pentoxide with alkylated hydroxy aromatic compounds, in which the alkyl groups are of relatively short chain length as compared to the wax group substituents of the wax alkylated hydroxy aromatic compounds used herein. As far as is known, however, products of the present type, i. e. wherein the alkyl substituent groups are of wax origin, have not been used in such applications heretofore and, in fact, have not been prepared heretofore.

In accordance with this invention, it has been found that the wax-alkylated phenol-phosphorus pentoxide products are unexpectedly superior to the products obtained by the reaction of the lower alkyl phenols with phosphorus pentoxide as addition agents for petroleum oil fractions, as will be demonstrated hereinafter. In particular, we have found that the wax-alkylated phenol-phosphorus pentoxide products are highly superior to the non-wax alkylated phenol-phosphorus pentoxide products as extreme pressure agents for mineral lubricating oils and as rust inhibitors in gasoline.

In preparing the products herein contemplated, the wax-alkylated hydroxy aromatic compound and the phosphorus pentoxide are heated together at a temperature of from about 50° C. to about 150° C. for a period of time sufficient to insure substantially complete reaction, usually from about 5 to about 15 hours. An inert solvent such as toluene, xylene or the like may be used to facilitate the reaction. A mineral lubricating oil may also be conveniently used as a solvent where the product is to be employed as a lubricating oil additive, since in this way a mineral oil concentrate of the product will result which is readily soluble in oil and at the same time the step of removing the solvent upon completion of the reaction is avoided. Where a solvent other than mineral oil is used, the reaction mixture is filtered and topped at elevated temperature and reduced pressure to remove the solvent.

The proportion of wax-alkylated hydroxy aromatic compound and phosphorus pentoxide used in the reaction can be varied between from about 1 to about 3 mols of the wax-alkylated hydroxy aromatic compound to 1 mol of phosphorus pentoxide, although the preferred products are obtained by the use of 3 mols of the wax-alkylated hydroxy aromatic compound per mol of phosphorus pentoxide.

The use of wax phenol as the wax-alkylated hydroxy aromatic compound reactant in the preparation of the additives herein contemplated is preferred. However, other wax alkylated hydroxy aromatic compounds may be satisfactorily used, such as alpha-naphthol, beta-naphthol, resorcinol, catechol, hydroquinone, alpha-anthrone, beta-anthrone and the cresols.

The exact nature of the products of the invention are not known, however, it may be stated, without intent to limit the invention, that they are believed to be mixtures of wax aryl-substituted phosphoric acids, such as mono- and di-wax aryl phosphoric acid and wax aryl pyrophosphoric acid. In order to more fully illustrate the manner of preparation of these products the following specific examples are presented.

PREPARATION OF WAX-PHENOL (3–14)

A paraffin wax melting at approximately 120° F. and predominantly comprised of hydrocarbons, having at least 20 and an average of about 24 carbon atoms in their molecules, is melted and heated to about 200° F., after which chlorine is bubbled therethrough until the wax has absorbed about 14%, by weight, of chlorine. A sufficient quantity of this chlorinated wax to provide 3 atomic proportions of chlorine is then heated to a temperature varying from just above its melting point to not over 150° F. One mol of phenol (C_6H_5OH) is then mixed with the chlorowax. The mixture is then heated to about 150° F. and a quantity of anhydrous aluminum chloride, corresponding to about 3% of the weight of the chlorowax in the mixture, is slowly added with active stirring. The rate of addition of the aluminum chloride should be sufficiently slow to avoid violent foaming and during the addition the temperature should be held at about 150° F. After the aluminum chloride has been added the temperature of the mixture may be increased slowly over a period of from 15 to 25 minutes to a temperature of about 250° F. and then should be more slowly increased to about 350° F. To control the evolution of HCl gas, the temperature of the mixture is preferably raised from 250° F. to 350° F. at a rate of approximately one degree per minute, the whole heating operation occupying approximately two hours from the time of adding the aluminum chloride. If the emission of HCl gas has not ceased when the final temperature is reached, the mixture may be held at 350° F. for a short time to allow completion of the reaction. However, to avoid possible cracking of the wax, the mixture should not be heated appreciably above 350° F., nor should it be held at that temperature for any extended length of time.

It is important that all unreacted, or non-alkylated, phenol remaining in the reaction mixture, as well as aluminum chloride, be removed. This can be conveniently effected by washing the product several times with

a mixture of water and an alcohol, such as butanol, preferably at elevated temperature, say 175° F. The product may then be treated with steam. This latter step will insure complete removal of the unreacted material and also dry the product.

It will be understood that a wax-substituted phenol prepared according to the above procedure in which a quantity of chlorowax containing three atomic proportions of chlorine and having a chlorine content of 14% is reacted with one mol of phenol, is designated as "wax-phenol (3–14)." Similarly, "wax-phenol (3–10)" and "wax-phenol (1-10)" may also be prepared by the reaction of sufficient amounts of chlorinated wax, containing 10 per cent by weight of chlorine, to provide 3 atomic proportions and 1 atomic proportion of chlorine per mol of phenol, respectively, in the reaction and are useful in the invention. In general, the amount of chlorowax, containing from about 10 to 18 per cent by weight of chlorine, used in the reaction is sufficient to supply between 1 and 4 atomic proportions of chlorine per mol of phenol used.

In preparing the "wax-phenol (1–10)" used in the following Examples V and VI, the procedure just described for the preparation of "wax-phenol (3–14)" was modified slightly in that an excess of phenol (100%) was used for reaction with the chlorowax (an amount to provide one atomic proportion of chlorine) in order to insure as complete a conversion as possible to monowax alkylated phenol.

Further details relative to the procedure for the preparation of wax phenols suitable for use herein may be had by reference to Patent No. 2,191,499, issued February 27, 1940, to Orland M. Reiff.

EXAMPLE I

Wax phenol (3–10)-P_2O_5 product (3:1)

Reaction mixture (mol ratio of wax phenol: P_2O_5=3:1)—

Wax phenol (3–10) (phenol content=approx. 9.0%)	grams	300
P_2O_5	do	14.0
Toluene	ml	300

The wax phenol (3–10) and toluene were placed in a 2-liter, 4-necked, round bottom flask equipped with a reflux condenser, thermometer and mechanically driven stirrer. After heating to 100° C., P_2O_5 was gradually added to the mixture over a 4-hour period. Following this, the temperature of the mixture was held at 100° C. for a period of 8 hours to insure complete reaction. The product was then filtered through "Hi-Flo," a diatomaceous earth filter aid, and the filtrate was topped to 150° C. under diminished pressure to remove the toluene solvent. The residue, representing the finished product, contained 1.77% phosphorus and had a neutralization number of 47.2.

EXAMPLE II

Wax phenol (3–14)-P_2O_5 product (3:1)

Reaction mixture (mol ratio of wax phenol: P_2O_5=3:1)—

Wax phenol (3–14) (phenol content=approx. 11.9%)	grams	300
P_2O_5	do	18
Toluene	ml	300

Procedure

Same as described in Example I. The product contained 2.2% phosphorus and had a neutralization number of 62.5.

EXAMPLE III

Wax phenol (3–14)-P_2O_5 product (2:1)

Reaction mixture (mol ratio of wax phenol: P_2O_5=2:1)—

	Grams
Wax phenol (3–14) (phenol content=approx. 11.9%)	200
P_2O_5	18
S. A. E. 20 mineral oil	200

Procedure

The wax phenol (3–14) and mineral oil were placed in a 1-liter, 4-necked, round bottom flask equipped with a reflux condenser, thermometer and mechanically-driven stirrer. After heating to 100° C., P_2O_5 was gradually added to the mixture over a 2½ hour period. Following this, the temperature of the mixture was maintained at 100° C. for an 8-hour period to insure complete reaction. The reaction mixture was then filtered through a layer of "Hi-Flo," a diatomaceous clay filter aid, contained in a heated Buchner funnel. The filtrate, representing the finished product, contained 1.53% phosphorus and had a neutralization number of 44.2.

EXAMPLE IV

Wax phenol (3–14)-P_2O_5 product (1:1)

Reaction mixture (mol ratio of wax phenol: P_2O_5=1:1)—

	Grams
Wax phenol (3–14) (phenol content=approx. 11.9%)	200
P_2O_5	36.0
S. A. E. 20 mineral oil	400

Procedure

Same as described in Example III. The product contained 2.02% phosphorus and had a neutralization number of 40.3.

EXAMPLE V

Wax phenol (1–10)-P_2O_5 product (3:1)

Reaction mixture (mol ratio of wax phenol: P_2O_5=3:1)—

Wax phenol (1–10) (phenol content=approx. 17.4%)	grams	400
P_2O_5	do	35.5
Toluene	ml	400

Procedure

Same as described in Example I. The product contained 2.96% phosphorus and had a neutralization number of 77.3.

EXAMPLE VI

Wax phenol (1–10)-P_2O_5 product (2:1)

Reaction mixture (mol ratio of wax phenol: P_2O_5=2:1)—

	Grams
Wax phenol (1–10) (phenol content=approx. 17.4%)	185
P_2O_5	24.4
Toluene	185

Procedure

Same general procedure as described in Example I. The product contained 4.59% phosphorus and had a neutralization number of 96.3.

EXAMPLE VII

192½ stock phenol (3–10)-P_2O_5 product (3:1)*

Reaction mixture (mol ratio of 192½ stock phenol: P_2O_5=3:1)—

	Grams
192½ stock phenol (3–10) (phenol content=approx. 7.6%)	500
P_2O_5	19
Toluene	500

Procedure

Same general procedure as described in Example I. The product contained 1.48% phosphorus and had a neutralization number of 52.4.

EXAMPLE VIII

192½ stock phenol (3–10)-P_2O_5 product (2:1)*

Reaction mixture (mol ratio of 192½ stock phenol: P_2O_5=2:1)—

	Grams
192½ stock phenol (3–10) (phenol content=approx. 7.6%)	500
P_2O_5	28.5
Toluene	500
S. A. E. 10 mineral oil	500

*A wax fraction derived from petroleum.

Procedure

The same general procedure as described in Example I was followed, with the exception that this product was diluted with mineral oil after removal of toluene, to reduce its viscosity and facilitate blending operations. The finished product contained 1.26% phosphorus and had a neutralization number of 33.8.

EXAMPLE IX

192½ stock phenol (2–10)-P_2O_5 product (3:1)*

Reaction mixture (mol ratio of 192½ stock phenol: P_2O_5=3:1)—

	Grams
192½ stock phenol (2–10) (phenol content=approx. 11.9%)	100
P_2O_5	6.0
S. A. E. 20 mineral oil	200

*A wax fraction derived from petroleum.

Procedure

Same general procedure as described in Example III. The product contained 0.65% phophorus and had a neutralization number of 28.2.

The following examples show the preparation of products of phosphorus pentoxide with alkylated phenols in which the alkyl substitutents are of non-wax origin. These products were used in the tests hereinafter described as a basis for comparing their effectiveness as petroleum additives with that of the wax phenol-phosphorus pentoxide products of the previous examples.

EXAMPLE X

Diamylphenol—P_2O_5 product (3:1)

Reaction mixture (mol ratio of diamylphenol: P_2O_5=3:1)—

	Grams
Di-tert-amylphenol	234
P_2O_5	27

Procedure

The diamylphenol was placed in a 1-liter, 4-necked, round bottom flask equipped with a reflux condenser, a thermometer, and a mechanically-driven stirrer. After heating to 95–100° C., P_2O_5 was gradually added over a 4-hour period. Following this, the temperature of the mixture was held at 95° C. for 2 hours and at 150° C. for 3½ hours. The product was then diluted with 150 ml. of benzene, filtered through "Hi-Flo" and topped to 180° C. under diminished pressure to remove the solvent. The residue, representing the finished product, contained 8.3% phosphorus and had a neutralization number of 213.

EXAMPLE XI

Dodecylphenol—P_2O_5 product (3:1)

Reaction mixture (mol ratio of dodecylphenol: P_2O_5=3:1)—

Dodecylphenol	grams	75
P_2O_5	do	13.6
Toluene	ml	50

Procedure

Same general procedure as described in Example I. The product contained 6.48% phosphorus and had a neutralization number of 190.

EXAMPLE XII

Trioctadecylphenol—P_2O_5 product (3:1)

Reaction mixture (mol ratio of trioctadecylphenol: P_2O_5=3:1)—

Trioctadecylphenol (phenol content=approx. 12.4%)	grams	75
P_2O_5	do	4.7
Toluene	ml	75

Procedure

Same general procedure as described in Example I. The product contained 1.83% phosphorus and had a neutralization number of 54.6.

EXAMPLE XIII

Octadecylphenol—P_2O_5 product (3:1)

Reaction mixture (mol ratio of octadecylphenol: P_2O_5=3:1)—

	Grams
Octadecylphenol	40
P_2O_5	5.0

Procedure

The octadecylphenol was placed in 250 ml., 4-necked, round bottom flask containing a reflux condenser, thermometer and mechanically-driven stirrer. After heating to 100° C., P_2O_5 was gradually added over a 20-minute period. The mixture was then heated for 6½ hours at 100° C. The reaction mixture was then filtered through "Hi-Flo" contained in a heated Buchner funnel. The filtrate, representing the finished product, contained 5.1% phosphorus and had a neutralization number of 141.

EVALUATION OF PRODUCTS

To demonstrate the effectiveness of the wax phenol-phosphorus pentoxide reaction products as extreme pressure agents and as pour point depressants in mineral lubricating oils, and particularly to show their superiority in these respects over the alkyl phenol-phosphorus pentoxide products in which the alkyl groups are of non-wax origin, oil blends of each of the products prepared in the foregoing examples were prepared and subjected to tests.

E. P. TEST

To determine their extreme pressure character, the oil blends were subjected to the Almen Pin test, described by Mougey and Almen, Proc. A. P. I. 1931, page 77. This test, which is designed to determine the ultimate load-carrying capacity of a lubricant, is widely used in the evaluation of E. P. lubricants. In this test the Almen test machine is used. The test lubricant is placed in a small metal cup with a one-fourth inch drill rod shaft rotating in a split bushing at 600 R. P. M. Weights are added at 10-second intervals to a loading lever working to apply pressure on the split bushing. The Almen value is expressed as the number of weights required to cause seizure of the bushing. Each weight weighs 2 pounds and is equivalent to 1,000 pounds per square inch pressure. Table I shows the results obtained in this test with the various oil blends. The oil was a solvent-refined, Mid-Continent, SAE 30 grade oil having a pour point of 20° F. and a kinematic viscosity at 210° F. of 11.96 cs.

Table I

Ex. No.	Product Blended in Oil	Mol Ratio, Phenol:P_2O_5	Concn. Wt. Percent (Undiluted Basis) [1]	Almen Value (Wts.)	A.S.T.M. Pour Point, ° F.	
					3% Wt. Concn. [1]	0.25% Wt. Concn. [1]
	None			2	+20	+20
I	Wax Phenol (3–10)-P_2O_5	3:1	3.0	12		−25
II	Wax Phenol (3–14)-P_2O_5	3:1	3.0	21	−30	−35
III	Wax Phenol (3–14)-P_2O_5	2:1	3.0	11	−30	−20
IV	Wax Phenol (3–14)-P_2O_5	1:1	3.0	10		−25
V	Wax Phenol (1–10)-P_2O_5	3:1	3.0	23	−25	+20
VI	Wax Phenol (1–10)-P_2O_5	2:1	3.0	11	−20	+20
VII	192½ Stk. Phenol (3–10)-P_2O_5	3:1	3.0	16	−25	−20
VIII	192½ Stk. Phenol (3–10)-P_2O_5	2:1	3.0	13	−30	−20
IX	192½ Stk. Phenol (2–10)-P_2O_5	3:1	3.0	13	−25	−15
X	Diamylphenol-P_2O_5	3:1	3.0	5	+20	+25
XI	Dodecylphenol-P_2O_5	3:1	3.0	6	+25	+20
XII	Trioctadecylphenol-P_2O_5	3:1	3.0	15	0	+20

[1] Reaction product undiluted with oil used as a solvent medium in the preparation thereof.

The test data in Table I illustrate the improvement in E. P. capacity of the oil, effected by the use of the wax-alkylated phenol-phosphorus pentoxide products over the products obtained with the alkylated phenols in which the alkyl substituent is of non-wax origin.

The data further show that the products derived from the wax phenol substituents are very effective as pour point depressants, whereas the products having the lower alkyl substituents are not.

To demonstrate the outstanding quality of the products of this invention as rust-inhibitors in gasoline, the products of several of the examples given hereinabove were subjected to the modified ASTM D 665–47–T test. The conditions of this test are recognized as being much more severe than actual pipeline conditions in that a much higher amount of water is present and it is generally accepted that test specimens exposed to the severe rusting conditions of this test for 48 hours are rusted to substantially the same degree as those exposed to a products pipeline for 30 to 60 days. The ASTM test used herein was modified to the extent of lowering the test temperature from 140° F. to 80° F. Briefly, this test involves stirring a mixture of 300 ml. of the gasoline under test with 30 ml. of dissolved water at a temperature of 140° F. with a cylindrical steel specimen immersed therein. After 48 hours contact with the gasoline-water mixture, the specimen is examined to determine whether or not it has rusted.

As is well known in the art, an important limitation upon the use of a rust-preventative in gasoline is its effect on gum formation. As a generalization, it can be said that rust-preventatives are non-volatile in nature and increase the amount of gum formed by the amount of preventative added. Consequently, a rust preventative useful in gasoline is one which is effective in concentration no greater than about 0.008 weight per cent non-volatile residue. When a sample of finished gasoline containing normal amounts of dye, tetraethyl lead, antioxidants, etc. and the indicated amounts of the products of the examples were subjected to the aforesaid ASTM test, the results obtained were as shown in Table II. It will be seen from the table that the wax-alkylated phenol-P_2O_5 products are much more effective as rust-preventatives in gasoline than the alkylated phenol-P_2O_5 products wherein the alkyl portions are of non-wax origin.

Table II

MODIFIED ASTM D 665-47-T TEST ON FINISHED MOBILGAS

Ex. No.	Product Added	Concentration Wt., Percent Active Ingredient							
		None	.0010	.0005	.0004	.00033	.0003	.00027	.0002
	None	Fail							
II	Wax Phenol (3-14)-P_2O_5 (3:1) Reaction Product		Pass			Pass		Pass	Fail.
I	Wax Phenol (3-10)-P_2O_5 (3:1) Reaction Product.			Pass	Pass		Pass		
X	Diamyl Phenol-P_2O_5 (3:1) Reaction Product.		Fail						
XI	Dodecyl Phenol-P_2O_5 (3:1) Reaction Product.			Fail					
XIII	Octadecyl Phenol-P_2O_5 (3:1) Reaction Product.			do	Fail				

The amount of the additive products of this invention to be added to the petroleum oil fraction will depend upon the particular fraction, i. e. whether a lubricating oil or a gasoline and, if a lubricating oil, on the particular improvement desired. Thus, as pointed out previously, when used in gasolines as rust inhibitors, the amounts are necessarily relatively small, the smallest effective amounts being the preferred amounts. In general, amounts within the range of from about 0.0003% up to about 0.008% are suitable. On the other hand, when utilized in lubricating oils as pour point depressants or extreme pressure additives larger amounts ranging from about 1% to about 5% are desirable, although amounts ranging from 0.25% up to about 10% may be used.

Concentrated oil solutions of the additives, containing from about 25 to about 75 per cent of the additives are also contemplated. Such concentrates are desirable for marketing, in that they save shipping space and provide a readily soluble form of the additive products for blending with oil in preparing the finished oil compositions.

The products of the invention may, of course, be used in petroleum oil fractions containing other additives designed to improve the character thereof in different respects, such as anti-oxidants, detergents, V. I. improvers, etc.

This invention is not intended to be limited in any way by the specific examples or illustrative procedures described herein, but only as indicated in the following claims.

I claim:

1. As a new composition of matter, the product obtained from the reaction involving 1 mol of phosphorus pentoxide with approximately 3 mols of wax phenol at a temperature of from about 50° C. to about 150° C.

2. A mineral lubricating oil containing a minor proportion, sufficient to improve the extreme pressure character and depress the pour point of said oil, of the product obtained from the reaction involving 1 mol of phosphorus pentoxide and approximately 3 mols of wax phenol at a temperature of from about 50° C. to about 150° C.

3. A gasoline containing a minor proportion, from about 0.0003% to about 0.008%, by weight, of the product obtained from the reaction involving 1 mol of phosphorus pentoxide and approximately 3 mols of wax phenol at a temperature of from about 50° C. to about 150° C.

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