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LUBRICATION

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This invention relates as indicated to lubrication, and more particularly to an improved composition of matter which may be employed as an addition agent to lubricating compositions generally, (1) for tht purpose of imparting thereto certain desirable characteristics such as (*a*) the ability to maintain lubrication under conditions of extreme pressure and (*b*) resistance to oxidation and the formation of sludge; and/or (2) the ability to impart (*a*) improved lubricating properties to lubricating compositions, while at the same time, (*b*) reducing the corrosive effect of the lubricant upon the bearings and associated metallic parts.

By "extreme pressures" are meant pressures of or substantially in excess of 10,000 lbs. per square inch, such pressures now being commonly encountered in hypoid gears, bearings, contact surfaces of cylinders and piston rings in internal combustion engines, and many other points. Such pressures between rubbing surfaces are being encountered with increasing frequency as the arts progress.

It is, therefore, the principal object of my invention to provide an addition agent for lubricating compositions which will improve the lubricating properties of such compositions with respect to one or more of the above-named desirable characteristics. Other objects of my invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain approved combinations of ingredients embodying my invention, such disclosed means constituting, however, but certain of various forms in which the principle of the invention may be used.

Broadly stated, this invention comprises the provision of addition agents for use in lubricating compositions, which addition agents may be described as reaction products of complex organic oils, fats, or waxes, with a phosphorus- and halogen-containing reagent.

In the foregoing definition of the generic invention there has been employed the term "complex organic oils, fats, or waxes." By this term, as used in the specification and in the claims, is meant that general class of products of which the specific examples hereinafter given are representative.

Inasmuch as the addition agents provided by this invention for use in lubricating compositions may be very conveniently and correctly described by having reference to their mode of preparation, i. e., the materials used in the reactions producing the addition agents, it is believed that the following classification of the reaction materials will describe the addition agents with sufficient accuracy.

The complex organic oils, fats and waxes which may be used in the preparation of addition agents contemplated by this invention may be classified as follows:

I. Complex organic oils
- A. Mineral origin
  - (1) Mineral oil of any origin, e. g.
    - Penna. (Preferred)
    - Mid-Continent
    - Coastal
    - including the following:
    - Mineral oil fractions
      - Kerosene
      - Gas oil
      - Solvent extracted fractions, such as furfural extract
    - Mineral lubricating oil fractions such as
      - Bright stocks
      - Neutral oils
  - (2) Oxidized mineral oils and fractions such as any of the materials listed under I A. (1) above, after heating from 100° C. to 200° C. and blowing with air for 20 to 100 hours; or prepared by any other method, as for example, Alox. (Burwell pat.)

B. Non-mineral origin
(1) Vegetable origin
Cottonseed oil
Corn oil
Castor oil
Soya bean oil
Rape seed oil
(2) Animal origin
Lard oil
Fish oils, e. g. Menhaden
Sperm oil

II. Waxes
A. Mineral origin
Paraffin wax
Montan wax
B. Non-mineral origin
(1) Vegetable waxes
Palm wax
Carnauba wax
Cottonseed wax
(2) Animal waxes
Beeswax
Rump gland wax
Spermacetti

The phosphorus- and halogen-containing reagents contemplated for use in my invention in providing the improved addition agents may be classified from the standpoint of the desirability of the products produced thereby according to the valency of the phosphorus, viz:

I. Valency of phosphorus three or less:

Phosphorus chloride	P_2Cl_4
Phosphorus trichloride	PCl_3
Phosphorus tribromide	PBr_3
Phosphorus tri-iodine	PI_3
Phosphorous oxy-chloride	$POCl$
Phosphorous sulpho-chloride	$PSCl$

Halogen derivatives of phosphine and organic substituted phosphines, e. g. phosphenyl chloride, $(C_6H_5)PCl_2$

II. Valency of phosphorus more than three:

Phosphorus pentachloride	PCl_5
Phosphorus dichlor-trifluoride	PCl_2F_3
Phosphorus trioxy-tetrachloride	$P_2O_3Cl_4$
Phosphorus oxychloride	$POCl_3$
Phosphorus oxybromide	$POBr_3$
Phosphorus thiochloride	$PSCl_3$
Phosphorus thiobromide	$PSBr_3$
Phosphorus thiobromide	$P_2S_3Br_4$
Phosphorus iodochloride	PI_2Cl_3
Phosphenyl oxychloride	$(C_6H_5)OPCl_2$

Of the improved addition agents provided by this invention, those formed from oils, fats, or waxes of mineral origin are usually to be preferred for the reason that the addition agents resulting therefrom are generally more resistant to oxidation and sludge-forming tendencies than those produced from oils, fats, or waxes of non-mineral origin.

The addition agents produced by reactions with reagents of the group in which the phosphorus has a valency of three or less are usually preferred for the reason that such addition agents, in general, produce desirable combinations of characteristics in the lubricant to which they are added in that the resulting lubricant is simultaneously particularly resistant to oxidation, as well as having a less corrosive effect on metallic bearings and associated parts as compared with the untreated lubricant.

A preferred class of addition agents for use in which oxidation or corrosion-inhibiting is of especial importance are those produced by the reaction of oils or waxes of mineral origin with a reagent in which the phosphorus has a valency of three or less for the reasons indicated above.

As a specific example of this last class of preferred addition agents, the following may be mentioned:

The product produced by reacting a refined mineral lubricating oil, preferably of Pennsylvania origin with phosphorus trichloride.

The procedure in producing such product is as follows:

In general, the reaction is carried out by adding to the complex organic oil, fat, or wax, hereinafter for convenience referred to as a complex oil, a minor proportion of the phosphorus and halogen-containing reagent. The exact proportion of the reagent will depend upon the nature of the oil and the reagent, in most cases being on the order of 5 to 30% by weight and preferably of a sufficient amount so that an excess will be present, as indicated by the presence of untreated reagent at the end of the reaction period.

The mixture is heated to a temperature of about 100° C., the exact temperature depending upon the boiling point of the reacting materials which, in the case of volatile materials, may make it necessary to heat under pressure. In most cases, atmospheric pressure may be employed and the reaction vessel provided with a reflux condenser to prevent loss of the reacting materials during the heating period.

In the case of certain of the less reactive reagents higher temperatures may be required to cause the desired reaction, for example, as high as 150° C. or even 200° C. or more.

In certain cases, it may be preferred to carry out the reaction in the vapor phase as, for example, by volatilizing the materials to be reacted and passing the mixed vapors through heated tubes or causing reaction to take place by means of other types of equipment or methods of promoting reaction.

The reaction period is preferably continued for about 1 to 10 hours; in most cases, three hours being a sufficient length of time. At the end of the reaction period, the product may be washed with water to decompose and remove the excess reagent, or it may be desirable to wash with solutions of alkalies or to treat with solid alkaline materials, especially where the reagent is of a more stable type.

After removal of the excess reagent, it is usually desirable to remove from the material such unstable or easily decomposed products as are still present. This may advantageously be done by blowing with steam, or treating with solutions of alkalies, or by heating with solid alkaline materials to a temperature of from 100° to 200° C.

The following example is given by way of illustration, only:

A Penna. bright stock is treated with about 20% by weight of phosphorus trichloride PCl_3, the mixture heated to boiling in a glass, or glass-lined, vessel provided with a reflux condenser, for about three hours. The product is washed with water and then blown with steam for about one-half hour and finally diluted with benzene to facilitate separation from the water layer; the benzene layer is then separated and the benzene removed by distillation, leaving the final product as the residue. The appearance and physical characteristics of the product thus ob-

tained are quite similar to that of the original bright stock. An analysis showed a chlorine content in the product of about 0.7%.

Another addition agent was prepared in exactly the same manner as above described using a Penna. neutral oil instead of a Penna. bright stock and the two resultant products were substantially equivalent in their physical characteristics and general effectiveness as addition agents.

Other addition agents were prepared by treating the following in a similar way with phosphorus trichloride:

Oxidized Penna. bright stock
Oxidized Penna. neutral oil
Furfural extract of mineral oil
U. G. I. gas oil

The addition agents contemplated for use in this invention may be added to any conventional lubricating oil, such as mineral oil (more specifically, motor oils), and may be employed in various combined oils so long as the remaining constituents are not incompatible with the addition agents herein defined. The concentration of addition agents found most useful in mineral lubricating oils will vary, for example, between about $\frac{1}{10}$ of 1% up to 2%; however, higher concentrations up to 20% may be employed for particular uses.

The presence of the named addition agents in substantial proportions in lubricating compositions generally, will usually improve certain properties such as the extreme pressure characteristics of the composition, even though the addition agent may be present over a wide range of concentrations. Corrosion tests on lubricants containing various concentrations of certain of the addition agents have shown, however, that for certain types of oil a low concentration, i. e., on the order of one-half percent or less, will markedly improve the corrosion characteristics of the lubricant; whereas, concentrations of 1% effect no improvement and may, in instances, increase the corrosiveness of the composition. In the case of other addition agents or other base oils concentrations of ½% may have no marked influence on the corrosion factor; whereas, concentrations of 1% have been found to materially improve the corrosive tendencies of the oil. In determining the concentrations which will produce the best results, tests may advantageously be conducted with the particular base oil to which the addition agents are to be added; however, with the foregoing explanation, it is believed that the workers in the art will be able to determine very readily the particular concentrations which produce the best results. For example, I have found that 1% of the addition agent produced, as previously explained, from Penna. bright stock or neutral oil, caused a very marked reduction in the corrosion of cadmium silver and lead bronze bearings exposed to a Penna. S. A. E. 10 motor oil for a period of 192 hours at a temperature of 150° C.

While it is believed that the film strength improving effect of the addition agents of this invention may be due to a chemical or physico-chemical action upon the metallic surface under conditions of extreme pressure, it is to be undertsood that this invention is not intended to be limited by any explanation or theory. The corrosion-inhibiting effect may be obtained either by protective action on the metal surfaces or a catalytic effect of the phosphorus in the composition, or the addition agent may react with the oil to render it relatively non-corrosive. The precise action is not known.

The following tables give the results of certain corrosion tests on different bearing alloys by the base oil and the same oil to which has been added different addition agents prepared as above explained.

Corrosion test—192 hours at 150° C.

Oil		Inhibitor, percent agent	Percent change in weight		
Type	S. A. E. No.		Cadmium-silver	Lead bronze	Babbitt
Pennsylvania	10	None	−0.12	−0.51	0.00
	10	¼ Neut.-PCl_3	−0.275	−0.48	−0.01
	10	½ Neut.-PCl_3	−0.00	−0.21	
	10	1 Neut.-PCl_3	−0.01	−0.05	
	10	¼ Br. St.-PCl_3	−1.43	−0.33	
	10	1 Br. St.-PCl_3	−0.04	−0.06	
	40	None	−0.03	−0.10	0.00
	40	¼ Neut.-PCl_3	−0.03	−0.16	0.00
	40	½ Neut.-PCl_3	−0.03	−0.05	−0.02
	40	¼ Br. St.-PCl_3	−0.42	−0.83	
	40	½ Br. St.-PCl_3	−0.01	−0.17	
	40	1 Br. St.-PCl_3	−0.04	−0.58	
Mid-Continent.	30	None	−0.00	−0.15	0.00
	30	¼ Neut.-PCl_3	−0.19	−0.15	
	30	½ Neut.-PCl_3	−0.13	−0.11	
	30	¼ Br.-St. PCl_3	−0.02	−0.10	
	30	½ Br.-PCl_3	−0.57	−0.02	
	30	1 Br. St.P-Cl_3	−0.32	+0.02	

It will be noted from the above table that when the correct percentages of addition agent are employed, the loss of weight of the bearings is as little or even less than when the untreated oils are used.

The following table indicates the results of certain well-known tests designed to show the condition of the oils at intervals during their use. It will be seen therefrom that the oils to which the addition agent has been added show marked improvements over the ordinary lubricating oils and a general resistance to deterioration.

"Indiana" oxidation tests

Oil	Type	Penn.	Penn.	Penn.	Penn.	Penn.	Penn.
	S. A. E. No.	10	10	10	40	40	40.
Inhibitor	Percent	None	1%	1%	None	½%	½%.
	Agent	None	Neut.-PCl_3*	Br. St-PCl_3*	None	Neut.-PCl_3	Br. St.-PCl_3.
Conradson carbon.	Original	0.18	0.14	0.18	1.33	1.35	1.21.
	100 hours	1.78	0.89	0.77	2.65	1.89	1.97.
Viscosity	Original	46.3	47.0	46.9	81.2	82.0	81.9.
	100 hours	52.9	48.8	48.9	104.5	93.0	94.3.
S. U. S. at 210° F.	Percent increase in viscosity at 100 hours.	14.2	3.8	4.2	28.7	13.4	15.1
Hours required for precipitation of—	10 mgs	32.5	87.0	82.5	More than 150.	More than 150.	More than 150.
	100 mgs	96.0	More than 150.	More than 150.			

*Neut.-PCl_3=Pennsylvania "150-neutral" treated with phosphorus trichloride. Br. St.-PCl_3=Pennsylvania bright stock treated with phosphorus trichloride.

"Indiana" oxidation tests

Oil	Type	Mid-continent	Mid-continent	Mid-continent	Mid-continent.
	S. A. E. No.	30	30	30	30.
Inhibitor	Percent	None	½%	½%	1%.
	Agent	None	Neut.-PCl_3	Br. St.-PCl_3	Br. St.-PCl_3.
Conradson carbon.	Original	0.68	0.39	0.49	0.47.
	100 hours	2.03	1.43	1.30	1.26.
Viscosity	Original	63.5	62.2	63.9	63.7.
	100 hours	76.1	63.9	68.9	68.7.
S. U. S. at 210° F.	Percent increase in viscosity at 100 hours.	19.8	9.8	7.8	7.8.
Hours required for precipitation of—	10 mgs	39.5	67.0	76.0	Approx. 170.
	100 mgs	97.0	145.0	76.0	Approx. 170.

NOTE.—Test was continued until amount of precipitate was at least 100 mg. in case this amount was precipitated in 150 hours or less. Otherwise test was discontinued at 150 hours.

The following is a description of an example illustrating the type of lubricating composition included in the present invention.

Fifty-five pounds of Pennsylvania Bright Stock were placed in an iron reactor equipped with a suitable heating device, agitator, cover, and reflux condenser. 1.1 pounds of phosphorus trichloride were added and heated to 180° C., and maintained at that temperature for about 1½ hours. The contents of the reactor were then cooled, transferred to a wooden tank, and diluted with about 7 gallons of benzol. About 7 gallons of water were placed in the same tank and the two layers thoroughly agitated together. The water was then allowed to settle and the water layer drawn off from the bottom of the tank. The water wash operation was repeated, and 1½ hours allowed for separation of the water layer before removing.

Low pressure steam was blown through the remaining product for two hours, after which the product was allowed to stand for about 48 hours to effect complete separation of the entrained water.

The benzol solution was then transferred to a glass-lined vacuum still and the benzol removed by distillation under a vacuum equivalent to 27" of mercury. The distillation was discontinued when the temperature of the liquid in the still reached 110° C.

The product thus obtained had the following characteristics:

Per cent free HCl	0
Per cent ash	.10
Per cent chlorine	.023
Per cent phosphorus	.046
Vis. at 210° F. in S. U. S.	148

This product was found to be a very effective oxidation inhibitor when incorporated, in an amount of about 1% or less, in various types of mineral lubricating oil. The oxidation inhibiting effect of this product was tested by means of a modified Indiana oxidation test in which the conditions were, in general, the same as those previously described for the Indiana oxidation test, with the exception that a coil consisting of 9 feet of 18 gauge iron wire, polished with emery cloth, was placed in the oxidation tube entirely submerged in the oil sample.

The results obtained with this test on three different types of oil, and the same oils containing 1% of the product prepared according to the above description, are shown in the following table:

	Pennsylvania SAE 10 motor oil		Pennsylvania SAE 40 motor oil		Mid-continent SAE 30 motor oil	
	No addition	+1% inhibitor	No addition	.5% inhibitor	No addition	.5% inhibitor
CONTINENTAL OXIDATION						
Conradson carbon:						
Original	.19	.15	1.30	1.01	.34	.11
At 48 hours	3.05	.75	2.58	1.49	2.32	1.26
Saybolt vis. at 210° F.:						
Original	46.5	46.7	82.9	83.9	63.5	64.0
At 48 hours	64.8	48.6	93.9	86.6	81.5	72.4
Percent vis. inc. at 48 hours	39.3	4.0	13.05	3.0	28.4	13.0
Naphtha insol. ppt.:						
Hrs. for 10 mgs	22.5	42.0	-------	-------	14.5	33.0
Hrs. for 100 mgs	40.5	-------	-------	-------	32.5	-------
Mgs. at 48 hrs	217.0	14.8	4.0	8.2	210	44.9
Acid number:						
Original	.17	.08	.04	.11	.04	.08
At 48 hours	2.23	.81	1.26	.37	1.38	.73
SHELL CORROSION						
Percent change in weight:						
Lead-bronze	−1.95	−.07	−.10	−.10	−.15	−.10
Babbitt	−.18	−.05	0	−.01	0	−.04

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the materials employed in carrying out the process provided the ingredient or ingredients stated in any of the following claims or the equivalent of such stated ingredient or ingredients be employed.

I, therefore, particularly point out and distinctly claim as my invention:

1. A lubricating composition comprising a mineral lubricating oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein from an effective amount to about 20%, based on the amount of mineral oil, of a composition selected from the following class;-the reaction product of a complex organic wax of mineral origin and a phosphorus-and-halogen-containing reagent in which the phosphorus has a valence of three or less; the reaction product of a complex organic oil of mineral origin and a phosphorus-and-halogen-containing reagent in which the phosphorus has a valence of three or less; the total amount of phosphorus in the lubricating composition being less than $\frac{1}{10}$% thereof.

2. An addition agent for lubricating compo-

sitions, comprising the reaction product of complex organic oil of mineral origin with a phosphorus-and-halogen-containing reagent in which the phosphorus has a valence of three or less, such product containing less than $\frac{1}{10}$% of phosphorus.

3. An addition agent for lubricating compositions comprising the reaction product of a complex organic wax of mineral origin with a phosphorus-and-halogen-containing reagent in which the phosphorus has a valence of three or less, such reaction product containing less than $\frac{1}{10}$% phosphorus.

4. A lubricating composition comprising a mineral lubricating oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein from an effective amount to about 20%, based on the amount of mineral oil, of the reaction product of a complex organic oil of mineral origin and a phosphorus-and-halogen-containing reagent in which the phosphorus has a valence of three or less, said reaction product containing less than $\frac{1}{10}$% phosphorus.

5. A lubricating composition comprising a mineral lubricating oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein from an effective amount to about 20%, based on the amount of mineral oil, of the reaction product of a complex organic wax of mineral origin and a phosphorus-and-halogen-containing reagent in which the phosphorus has a valence of three or less, said reaction product containing less than $\frac{1}{10}$% phosphorus.

6. A lubricating composition comprising a mineral lubricating oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein from about 0.1% to about 2%, based on the amount of mineral oil, of the reaction product of a complex organic oil of mineral origin and a phosphorus-and-halogen-containing reagent in which the phosphorus has a valence of three or less, said reaction product containing less than $\frac{1}{10}$% phosphorus.

7. An addition agent for lubricating compositions comprising the reaction product of a complex organic oil of mineral origin with a phosphorus-and-chlorine-containing reagent in which the phosphorus has a valence of three or less, the total phosphorus content of such reaction product being less than $\frac{1}{10}$%.

8. An addition agent for lubricating compositions comprising the reaction product of mineral oil with a phosphorus-and-halogen-containing reagent in which the phosphorus has a valence of three or less, said reaction product having a phosphorus content of less than .05%.

9. A lubricating composition comprising a mineral lubricating oil with the ability of such composition to resist oxidation improved by incorporating therein a small amount, based on the amount of mineral oil, of the reaction product of a complex organic oil of mineral origin with a phosphorus-and-chlorine-containing reagent in which the phosphorus has a valence of three or less, said reaction product containing less than about .05% phosphorus.

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