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MINERAL OIL COMPOSITIONS AND METHODS OF SUPPRESSING FOAMING IN OILS

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2 Claims. (Cl. 252—51)

This invention relates to mineral oil compositions and methods of suppressing foaming in oils.

In lubricating machinery with oils, and in handling oils as by pumping, conditions are often such that the oil is subjected to violent agitation in the presence of air; conditions such as to produce foam or froth. In some cases foaming or frothing is quite objectionable. For example, in lubricating automobile gearing (in the gear box, and rear axle) foaming produced by the churning of the gears gives rise to excessive leakage and loss of lubricant past retainer rings, etc. Moreover, foaming seriously interferes with the proper functioning of the oil. Automobile gears such as those used in transmission and differential gear assemblies often operate at very high speeds, as well as under high tooth pressures; therefore they require a very good lubricant to prevent or retard excessive wear due to metal-to-metal contact, and foaming is undesirable. The lubricants employed are viscous oils, often containing a so-called extreme pressure agent to assist in maintaining an oil film between the teeth; sulfurized sperm oil being especially good. If the lubricant contains air dispersed through it, it lacks proper film forming properties. Also in reduction gears, particularly herringbone gears, oil aerofoam is undesirable. Moreover foaming oil is much less effective to conduct heat away from the working zone. These difficulties are often aggravated by the fact that some extreme pressure agents present in the oil actually increase the foaming characteristics of the oil composition.

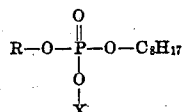
Foaming is also objectionable in other situations; for example, in compounding oils with extreme pressure agents and other additives, an operation involving thorough agitation. Nearly all petroleum oils foam to some extent under violent agitation. The more viscous the oil, the greater the amount of foam and the longer it persists after agitation is stopped.

In pumping oils with rotary gear, displacement, or other type pumps, foam or gas pockets often interfere with the pumping of the oil, causing a reduction in the stream of oil flow. This condition may be caused by either the vacuum on the intake or by the entrainment of gas due to violent agitation. In placing oil under vacuum, it sometimes is found that the characteristics of the oil are such as to cause foaming and loss of oil en-

trained in the gas removed. This loss of oil is objectionable. Moreover, as an airplane climbs to high altitudes, the temperature and pressure of the oil may be decreased, conditions which promote foaming tendencies.

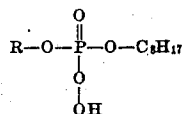
Among the objects of our invention are the provision of a method whereby foaming or frothing of oils as described is suppressed; and the provision of gear lubricants and other lubricating compositions which are characterized by freedom from tendency to foam or froth even under severe conditions.

We have discovered that foaming of petroleum oils can be suppressed or prevented by incorporating in the oil a small proportion of certain organic ammonium salts of acid octyl phosphate esters. These anti-foam agents are organic ammonium phosphates having the following formula:



wherein R represents an alkyl group containing 1 to 18 carbon atoms and X represents an organic ammonium group derived from a tertiary amine selected from the class consisting of heterocyclic nitrogen bases and dialkyl aryl amines.

That is, our new anti-foam agents are addition salts of said amines and acid dialkyl phosphate esters wherein at least one of said alkyl groups is an octyl group. In fact, they can be readily prepared by reacting either heterocyclic nitrogen bases or dialkyl aryl amines with various acid octyl phosphate esters having the formula:



wherein R represents an alkyl group containing 1 to 18 carbon atoms, including both straight-chain and branch-chain alkyl groups. Such methods of preparing these anti-foam agents are further illustrated post. These organic ammonium phosphates may also be prepared by other suitable methods.

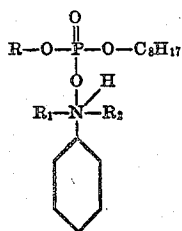
For example, dimethylaniline dioctyl phosphate

is a very good foam inhibitor. The addition salts of acid dioctyl phosphate with other dialkyl-anilines are also useful anti-foam agents.

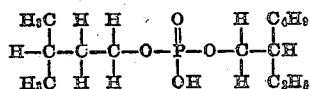
Likewise, dialkyl-aniline salts of other acid phosphate esters containing an octyl group and another alkyl group, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, amyl, isoamyl and the like, are also effective anti-foam agents for the present purposes. Those containing branch-chain alkyl groups are very effective foam inhibitors.

For example, a small proportion of dimethylaniline isoamyl octyl phosphate is most effective. Again, the diethylaniline salt of isoamyl octyl phosphate is also an excellent foam inhibitor. In our copending application Serial No. 453,458, filed August 3, 1942, we have specifically claimed improved mineral oil compositions containing the dimethylaniline and diethylaniline salts of isoamyl octyl phosphate, as the anti-foam agent. The present application is a continuation-in-part of said prior application Serial No. 453,458.

In general, the organic ammonium phosphates having the formula



wherein R, R₁ and R₂, respectively, represent alkyl groups which may be similar or dissimilar, are effective in suppressing the foaming of mineral oils and oil compositions; the dialkylaniline salts prepared from isoamyl octyl acid orthophosphate having the following formula



being particularly effective and advantageous as described in said prior application Serial No. 453,458. As a class these anti-foam agents are useful in the practice of the present invention.

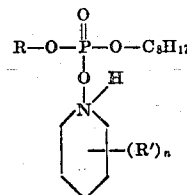
Further, the addition salts of said acid octyl phosphate esters and tertiary amines containing a heterocyclic nitrogen ring in the molecule thereof, are also effective foam suppressors. For instance, the organic ammonium octyl phosphate salts prepared from pyridine and alkyl-substituted pyridines, such as the picolines, lutidines, collidines, etc., are useful anti-foam agents.

For example, pyridine isoamyl octyl phosphate is an excellent foam suppressor in mineral oils and oil compositions. Improved mineral oil compositions containing this anti-foam agent are specifically claimed in our copending application Serial No. 459,179, filed Sept. 21, 1942.

The organic ammonium octyl phosphate salts prepared from the methyl pyridines, such as picolines, lutidines, etc., are also effective anti-foam agents. For example, 2,6-dimethyl-pyridine isoamyl octyl phosphate is most effective. Likewise, the other lutidine salts thereof are also excellent anti-foam agents. Improved mineral oil compositions containing lutidine isoamyl octyl phosphates, as the anti-foam agent, are specifically claimed in our copending application Serial No. 459,180, filed Sept. 21, 1942.

Again, the monomethyl pyridine salts of isoamyl octyl phosphate and other acid octyl phosphate esters are good anti-foam agents. In fact, the alpha-picoline salts of isoamyl octyl phosphate and dioctyl phosphate, respectively, are most effective. Likewise, the beta and gamma picoline salts of these acid octyl phosphates are good foam inhibitors.

Generically, these addition salts of acid octyl phosphate esters with pyridine and alkyl-pyridines may be represented by the following formula

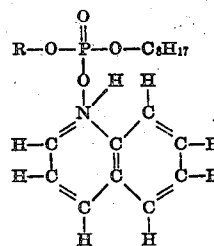


wherein R and R', respectively, represent alkyl groups which may be similar or dissimilar and n is from 0 to 5. As a class, these salts are useful and advantageous anti-foam agents.

Another advantageous class of anti-foam agents is the organic ammonium octyl phosphate salts prepared by reacting said acid octyl phosphate esters with other substituted heterocyclic nitrogen bases, such as quinoline, nicotine, etc., containing cyclic substituents attached to the heterocyclic ring thereof. That is, useful anti-foam agents can be prepared from complex nitrogen bases, as well as from tertiary amines having a single, simple heterocyclic nitrogen ring.

For example, quinoline isoamyl octyl phosphate is an excellent foam inhibitor. Improved mineral oil compositions containing this anti-foam agent are specifically claimed in our copending application Serial No. 454,460, filed August 11, 1942.

Another advantageous anti-foam agent is quinoline dioctyl phosphate. Likewise, the quinoline salts of other acid octyl phosphate esters are also effective foam inhibitors. As a class, these quinoline salts may be represented by the following formula:



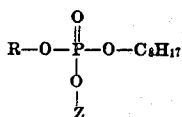
wherein R represents an alkyl group.

In other words, the heterocyclic nitrogen ring in our organic ammonium octyl phosphate salts may be further substituted; even with complex substituents such as cyclic groups, as well as simple methyl or alkyl groups as shown ante.

For instance, the nicotine salts of these acid octyl phosphate esters are also useful anti-foam agents. For example, the nicotine salts of isoamyl octyl phosphate and dioctyl phosphate, respectively, are effective foam suppressors. That is, our anti-foam agents can also be prepared from complex heterocyclic nitrogen bases containing a plurality of heterocyclic nitrogen rings. In this way, complex organic ammonium octyl phosphate salts are obtained.

Generically, these addition salts of acid octyl

phosphate esters with heterocyclic nitrogen bases may be represented by the following formula:



wherein R represents an alkyl group and Z represents an organic ammonium group derived from a heterocyclic nitrogen base. As a class, these organic ammonium octyl phosphate salts containing a heterocyclic nitrogen ring, are useful anti-foam agents. They may be employed with advantage in the practice of the present invention; this application being a continuation-in-part of said application Serial No. 454,460, as well as our prior applications Serial Nos. 459,179 and 459,180.

As shown in our Serial No. 453,458 and other prior copending applications, these anti-foam agents are quite different from the agents or additives previously employed in mineral oils and oil compositions. In general, as there stated, dissolving almost any additive in oil has a tendency to increase foaming more or less.

On the other hand, our new agents or compounds are remarkable in that they suppress foaming, even when present in small amounts, say 0.01 to 1.0 per cent by weight of the composition. They have no deleterious effect on the lubricating or other properties of the oil.

Our agents can be incorporated in all sorts of oils, to achieve the stated results. One particularly advantageous field of use is in gear lubricants for automobiles and the like. As stated, these lubricants are viscous and they contain extreme pressure agents or other additives; both of which facts make for heavy foaming. By dissolving a fraction of a per cent of our agent in such lubricants, foaming is prevented. For example, such a gear lubricant, within the purview of our invention, has the following compositions (per cent by weight):

Refined high-viscosity, lubricating oil	89 to 95.0
Refined sulfurized sperm oil	5 to 10.0
Dimethylaniline dioctyl phosphate	0.01 to 1.0

In the above composition, any of the organic ammonium octyl phosphates described ante may be used, in lieu of dimethylaniline dioctyl phosphate, as the anti-foam agent to obtain other advantageous gear lubricants.

Another field of use is in light (low viscosity) oils used in so-called fluid drives or in hydraulic drives. With these light oils (which are often of viscosity as low as SAE 10 grade) agitation may produce considerable foam, even though the foam subsides very quickly on ceasing agitation. Our new agents are also useful in cutting oils and indeed in any oil or oily composition, whether used as a lubricant or not, in which it is desired to prevent foaming.

The proportion of anti-foam agent to be dissolved in the oil or oil base depends on the viscosity of the oil, its ingredients and severity of the conditions of use. Ordinarily, 0.01 to 1.0 per cent of these agents by weight on the oil are employed; these organic ammonium octyl phosphate salts being very effective agents for the present purposes.

Our new agents can be readily prepared from various acid octyl phosphate esters and heterocyclic nitrogen bases or dialkyl aryl amines, as stated above. In one advantageous method of

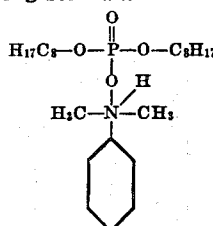
preparing these agents, the selected amine and acid octyl phosphate ester are reacted together to obtain an organic ammonium phosphate salt thereof; the reaction mixture being adjusted within the pH range of 2.0 to 5.5 in so preparing and recovering the amine salt. For example, dimethylaniline is brought into reaction with isoamyl octyl acid ortho-phosphate, and the pH of the reaction mixture is adjusted to within the range 2 to 4. With theoretical molecular ratio of the two reactants 1:1, the product is apt to be slightly too acid, with a pH below 2, and this is taken care of by using a slight excess of dimethylaniline so that the molecular ratio is between 1:1 and 1:1.1. Other useful anti-foam agents can be prepared in a similar manner by reacting various acid octyl phosphates with dimethylaniline or other tertiary amines of the classes described ante, to obtain organic ammonium salts thereof.

In general, the reaction products so obtained are oily materials which are readily soluble in oils. Thus, dissolving them in oils and oil compositions is very simple. As they readily dissolve in oils and oil compositions, our new agents can be easily incorporated and blended in mineral lubricating oils and oil compositions, particularly in the proportions described ante.

Many of the organic ammonium salts of acid octyl phosphate esters which are disclosed herein are new chemical compounds. The dialkyl aryl amine salts of isoamyl octyl phosphate are claimed as new chemical compounds in our copending application, Serial No. 639,701, filed on January 7, 1946. The tertiary heterocyclic nitrogen base salts of isoamyl octyl phosphate are claimed as new chemical compounds in our copending application, Serial No. 640,666, filed on January 11, 1946, as a continuation-in-part of the present application.

The following example illustrates the preparation of a gear lubricant in accordance with the present invention.

Example I.—A highly viscous, highly refined Pennsylvania oil was selected as the base and in it was dissolved 0.04 per cent of dimethylaniline dioctyl phosphate; this anti-foam agent having the following formula



and being an addition salt of dimethylaniline and acid dioctyl phosphate.

To evaluate the foaming properties of the straight oil and the improved oil samples (500 cc.) of the two oils were subjected to foam test No. 1 (described post). The results were as follows:

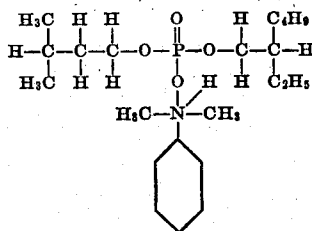
Composition	Straight oil	Improved oil
End of stirring (15 minutes):		
Temperature, °F	84	81
Oil-foam, cc.	1,700	520
Ratio of volume of oil-foam to the volume of the original oil	3.40	1.04
After 1 hr. standing:		
Temperature, °F	77	77
Oil-foam, cc.	660	500
Ratio of volume of oil-foam to the volume of the original oil	1.32	1.0
Nature of foam	Fine	No foam

It will be observed that the improved oil composition so prepared has marked resistance to foaming as compared to the straight oil.

In the above example, other dialkylaniline salts of dioctyl phosphate may be employed as the foam suppressor. Again, the addition salts of acid dioctyl phosphate with heterocyclic nitrogen bases may be used as the anti-foam agent in these oil compositions.

The following example illustrates the preparation of another gear lubricant in accordance with the present invention.

Example II.—A highly viscous, highly refined Pennsylvania oil was selected as the base and in it was dissolved 0.04 per cent of dimethylaniline isoamyl octyl phosphate; this anti-foam agent having the following formula



and being an addition salt of dimethylaniline and acid isoamyl octyl ortho-phosphate.

As shown in the following table, the change in viscosity and in color by incorporation of the agent was negligible.

	Straight oil	Improved oil
Gravity, °API.....	26.6	26.5
Viscosity, SUV:		
100° F.....	1,918	1,905
210° F.....	141.7	142.2
Color, NPA.....	4.75	4.75

To evaluate the foaming properties of the straight oil and the improved oil, samples (500 cc.) of the two oils were subjected to foam test No. 1 (described post). The results were as follows:

Composition	Straight oil	Improved oil
End of stirring (15 minutes):		
Temperature, °F.....	84	83
Oil+foam, cc.....	1,740	540
Ratio of volume of oil+foam to the volume of the original oil.....	3.48	1.08
After 1 hr. standing:		
Temperature, °F.....	77	77
Oil+foam, cc.....	660	500
Ratio of volume of oil+foam to the volume of the original oil.....	1.32	1.0
Nature of foam.....	Fine	No foam

It will be noted that the straight oil developed more than twice its volume of foam under the conditions of the test and that an appreciable volume of foam remained even after an hour's standing; while the improved oil developed only a negligible amount of foam, which was all gone at the end of an hour.

Decreasing the percentage to 0.01 still leaves the oil much less susceptible to foaming than the straight oil.

This foam suppressor as stated can be added to compounded lubricants to prevent foaming thereof. It is compatible with most of the other types of improvement agents now employed and the amount required to prevent foaming in such compounded lubricants is relatively small and

does not deleteriously affect the other properties of compounded lubricants. This is an important part of the invention, as certain of the agents employed to impart particular properties to lubricating oils have been found also to promote the foaming of the oil composition when agitated. By adding even traces of the present foam suppressor, such compounded lubricants become very resistant to foaming, even under drastic service conditions.

In making up compounded lubricants of this type it is advantageous to dissolve the amino-phosphate in the oil first, as thereby foaming is prevented during the step of mixing in the extreme pressure agent or other additive. But so far as performance of the lubricant in service is concerned, the order of addition makes no difference.

The following example illustrates the properties of an extreme pressure gear lubricant prepared in accordance with the invention.

Example III.—A conventional gear lubricant contains 92.5 per cent by volume of a highly refined, viscous Pennsylvania oil and 7.5 per cent of refined sulfurized sperm oil (Smith and Cantrell Patent 2,179,064). A similar lubricant prepared according to the invention contains these oils in proportions 92.46 and 7.5 per cent respectively and 0.04 per cent of dimethylaniline salt of acid isoamyl octyl phosphate; this anti-foam agent being the same as employed in Example II ante.

The viscosity of the conventional lubricant was 1918 SUV at 100° F., 767 at 130° F., and 141.7 at 210° F. The viscosity of the improved lubricant was only negligibly different from this, and the same was true of the other characteristics—gravity, viscosity index, flash and fire tests, pour test, color, sulfur, copper strip tests, centrifuge test (for gravity-separable matter), and carbon residue. The neutralization number of the new lubricant was 0.56 against 0.50 for the old. The surface tensions were nearly identical. The Almen and Timken tests, indicative of the lubricating value of the oil, as secured on the compounded oil before the addition of the foam suppressing agent, were the same as the corresponding tests made after the addition of the indicated amount of this foam suppressor.

In other words, the characteristics of the two lubricants were practically the same, except for the foaming properties. The following are comparable tests (the nature of which is described in detail below) on these properties. The samples were 500 cc. each, the speed of the agitators 550 R. P. M. and the initial temperature 77° F.

Foam tests

	Old lubricant	New lubricant	
After stirring for.....	15 min.	15 min.	44 hr.
Temperature, °F.....	84	83	83
Oil+foam, cc.....	1,740	540	580
Vol. of oil+foam.....	3.48	1.08	1.18
Vol. of oil.....			
After standing 1 hr. after stirring stopped:			
Temperature, °F.....	77	77	77
Oil+foam, cc.....	660	500	540
Vol. of oil+foam.....	1.32	1.00	1.08
Nature of foam.....	Coarse	None	

To evaluate the foaming tendency of petroleum oils and compositions a test was devised which affords an exceptionally accurate indica-

tion of the comparative foaming tendencies. A sample of oil is subjected to very drastic foaming conditions under a standardized procedure which makes it possible to determine quantitatively the tendency of the oil to foam and the stability or permanency of the foam produced. In general it resembles a somewhat similar testing method employed by the General Motors Corporation for determining the foaming tendencies of gearing lubricants, but has been modified in the direction of greater accuracy and in order to make it possible to record more comprehensible test data.

Foaming test (No. 1)

An agitating means is provided which is an adaptation of an ordinary commercial motor-driven household mixer—a "Sunbeam Mixmaster," Model 1, manufactured by the Flexible Shaft Company, Chicago, Ill. The device employed in the test is the usual household model with two slight changes: the turntable of the usual household mixer is replaced by a rigid platform, and a cylindrical brass container having an inside diameter of 7 inches and an inside height of 4 inches is substituted for the usual household glass mixing bowl. The container is fitted with a gage for measuring the depth of oil or oil and foam therein before and after agitation.

The agitator device itself comprises a pair of motor driven beaters which are of the convex outside surface type as described in U. S. Patent 2,161,881, each beater having a pair of blades of the type indicated and being so positioned with respect to each other that the two pairs of beater elements are at right angles and rotate in opposite directions in closely spaced, overlapping paths. In operating position, the beaters are perpendicular to the base of the mixer, as shown in Patent 2,161,881. In the present test they are centered in the container and the bottom of the beaters is spaced approximately $\frac{1}{8}$ inch from the bottom of the pan when the latter is positioned on the rigid platform. With 500 cc. of oil in the container, the beaters are submerged in the initial oil sample only to a depth of $\frac{3}{4}$ of one inch. The beaters are rotated at a speed of 550 R. P. M. controlled within ± 10 R. P. M.

A measured sample of 500 cc. (± 5 cc.) of oil is introduced into the container, the temperature of the sample is brought to 77° F. and the container is then placed in position and the heater elements lowered into operating position.

The motor is started and adjusted to the speed indicated above. The beaters agitate the oil and beat air into the sample. Agitation is continued for exactly 15 minutes.

The motor is now stopped, the beaters are removed from the oil, and any oil or foam adhering to the beaters is permitted to drain into the container, which takes one or two minutes. The foam level is then immediately determined, and the temperature of the sample is measured. It is then possible to calculate the ratio of the volume of oil and foam to the volume of the original oil, with correction for any temperature changes.

The container is removed and allowed to stand quiet for one hour (measured from the time the stirring is stopped). The volume and temperature measurements are taken again, and serve to indicate stability or permanence of the foam produced.

Of course, the test procedure may be varied, as for example by changing the size of the sample,

the speed or agitation or the time of agitation, or by taking the final measurements at an earlier or later period. However, in the test referred to in the specific examples ante, the procedure was precisely as indicated.

Test No. 2 is the same as test No. 1 except that agitation is continued for 44 hours instead of 15 minutes. (Longer periods of agitation may be employed if a still more drastic test is required.)

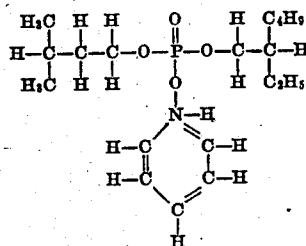
In some very low viscosity oils considerable foam may develop during agitation, which disappears very quickly when agitation is stopped. These conditions are found, for example, in marine turbine lubrication systems (which use light oils) at the point where returned oil is discharged violently into a reservoir. To evaluate foaming in such cases there is employed a third test No. 3, similar in all respect to test No. 1, except that the measurements of oil and foam are made while the motor is still running. The following example shows how a turbine oil treated according to the invention behaves under such conditions.

Example IV.—A highly refined Pennsylvania turbine oil was subjected to test No. 3. After 15 minutes agitation on oil plus foam measured 800 cc. as compared with 500 cc. for the original oil.

The same oil after treating with 0.01 per cent of dimethylaniline isoamyl octyl phosphate tested only 540 cc. for the oil plus foam.

In the foregoing Examples II, III and IV, we have illustrated certain embodiments of our invention employing dimethylaniline isoamyl octyl phosphate which is an excellent and advantageous agent for the purposes of this invention. However, as described ante, we may also employ with advantage other amine salts of isoamyl octyl phosphate prepared by reacting the acid phosphate ester with various amines, such as diethylaniline, pyridine, picoline, lutidine, quinoline, nicotine, and other aromatic heterocyclic amines having one or more rings. These amines are well known compounds and are commercially available and can be readily converted into agents suitable for the present purposes. The amine salts so obtained may be used in lieu of the dimethylaniline isoamyl octyl phosphate in the examples given ante. Such additional embodiments of our invention are further illustrated in the examples given post, which illustrate other advantageous ways of practicing this invention.

Example V.—Another improved gear lubricant was prepared as follows: A highly viscous, highly refined Pennsylvania oil was selected as the base and in it was dissolved 0.04 per cent of pyridine isoamyl octyl phosphate; this anti-foam agent having the following formula:



and being an addition salt of pyridine and acid isoamyl octyl phosphate.

The foaming properties of the straight oil and

the improved oil, as measured by foam test No. 1, were as follows:

Composition	Straight oil	Improved oil
At end of stirring (15 minutes):		
Temperature, °F.....	84	83
Volume of oil and foam, cc.....	1,756	540
Ratio ¹	3.52	1.08
After 1 hr. standing:		
Temperature, °F.....	77	77
Volume of oil and foam, cc.....	670	500
Ratio ¹	1.34	1.00
Nature.....	Fine	No foam

¹ Ratio of $\frac{\text{volume of oil and foam}}{\text{volume of original oil}}$

It will be noted that the straight oil developed more than twice its volume of foam and that an appreciable volume of foam remained even after one hour standing; while the improved oil developed only a negligible amount of foam which was all gone at the end of an hour.

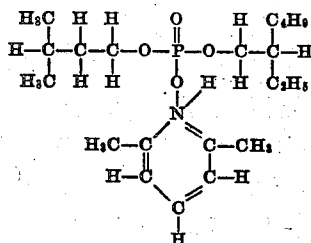
In the above example, decreasing the percentage of anti-foam agent to 0.01 per cent still leaves the oil much less susceptible to foaming than the straight oil. That is, pyridine isoamyl octyl phosphate is a very effective foam inhibitor. Accordingly, it is also useful and advantageous, as a foam suppressor, in compounded gear lubricants and in turbine oils such as shown in Examples III and IV ante. In fact, as shown by various foam tests, pyridine isoamyl octyl phosphate also effectively suppresses foaming in such compositions.

Further, in such compositions, other addition salts of acid isoamyl octyl phosphate and pyridine compounds containing substituent groups attached to the pyridine ring thereof, may be used as the anti-foam agent. The improved oil compositions so obtained are also advantageous in the practice of this invention.

Typical examples of these advantageous compositions are as follows:

Example VI.—A highly refined Pennsylvania turbine oil was subjected to test No. 3. After 15 minutes agitation, the oil plus foam measured 800 cc. as compared with 500 cc. for the original oil. The same oil after treating with 0.01 per cent of 2,6-lutidine isoamyl octyl phosphate showed only 540 cc. of oil plus foam.

This advantageous anti-foam inhibitor has the following formula

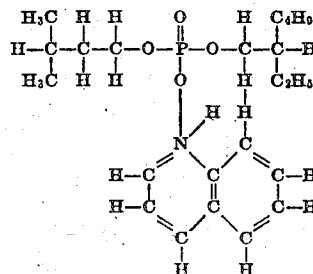


and can be readily prepared by reacting 2,6-lutidine with acid isoamyl octyl phosphate as described ante.

In the practice of our invention, other lutidines may be used in lieu of 2,6-lutidine in forming our new agents, and the lutidine octyl phosphate compounds so obtained are likewise excellent foam suppressors. They may also be employed in making improved lubricants similar to those illustrated in the example ante. Further, the octyl phosphate salts of other substituted pyridine compounds are also useful anti-foam agents. For instance, they are advantageous in preparing im-

proved gear lubricants in accordance with this invention, as illustrated in the following example:

Example VII.—A highly viscous highly refined Pennsylvania oil was selected as the base and in it was dissolved 0.04 per cent of quinoline isoamyl octyl phosphate; this anti-foam agent having the following formula



and being an addition salt of quinoline and acid isoamyl octyl phosphate.

The foaming properties of the straight oil and the improved oil, as measured as foam test No. 1 were as follows:

Composition	Straight oil	Improved oil
At end of stirring (15 minutes):		
Temperature, °F.....	84	83
Volume of oil and foam, cc.....	1,756	540
Ratio ¹	3.51	1.08
After 1 hr. standing:		
Temperature, °F.....	77	77
Volume of oil and foam, cc.....	670	500
Ratio ¹	1.34	1.0
Nature.....	Fine	No foam

¹ Ratio of $\frac{\text{volume of oil and foam}}{\text{volume of original oil}}$

It will be observed that the straight oil developed more than twice its volume of foam under the conditions of the test and that an appreciable volume of foam remained even after one hour's standing, while the improved oil developed only a negligible amount of foam, which was all gone at the end of one hour.

In the above example, the addition salts of other acid octyl phosphate esters, such as dioctyl phosphate etc. etc., with quinoline may also be used as the anti-foam agent to produce still other advantageous gear lubricants. Likewise, the salts of acid octyl phosphate esters with other complex heterocyclic nitrogen bases may be used in making such lubricants. For instance, nicotine isoamyl octyl phosphate may be employed with advantage as the foam inhibitor. This anti-foam agent is also advantageous in preparing gear lubricants as illustrated in the following example.

Example VIII.—Another improved gear lubricant made according to this invention was prepared by incorporating 0.04 per cent of nicotine isoamyl octyl phosphate in a modern commercial gear lubricant containing 92.0 per cent by volume of highly refined viscous Pennsylvania oil and 8.0 per cent of a special synthetic mixture containing around 10 per cent of sulfur.

The viscosity of the improved lubricant was only negligibly different from the original oil, and the same was true of the other characteristics—gravity, viscosity index, flash and fire tests, pour test, color, sulfur, copper strip tests, centrifuge test (for gravity-separable matter), and carbon residue. The neutralization number of the improved lubricant was 0.45 compared to 0.42 for the old. The surface tensions were

nearly identical. The Almen and Timken tests, indicative of the lubricating value of the oil, as secured on the compounded oil before the addition of the foam suppressing agent, were the same as the corresponding tests made after the addition of the indicated amount of this foam suppressor.

In other words, the characteristics of the two lubricants were practically the same except for the foaming properties which were as follows:

Foam tests

	Old lubricant		New lubricant	
	15 min.	15 min.	44 hr.	
After stirring for.....	84	83	83	
Temperature, ° F.....	1,750	540	590	
Oil+foam, cc.....	3.49	1.08	1.18	
Ratio of volume of oil+foam to the volume of original oil.				
After 1 hr. standing:	77	77	77	
Temperature, ° F.....	665	500	500	
Oil+foam, cc.....	1.33	1.00	1.00	
Ratio of volume of oil+foam to the volume of the original oil.				
Nature of foam.....	Fine	None	None	

In the above test, the samples were 500 cc. each, the speed of the agitators 550 R. P. M. and the temperature 77° F.

Likewise, the addition salts of other complex heterocyclic nitrogen bases may be employed in the above example as the foam agent in lieu of nicotine isoamyl octyl phosphate.

That is, as shown in the foregoing specific examples, the addition salts of acid isoamyl octyl phosphate with tertiary amines of the class consisting of dialkylaryl amines and heterocyclic nitrogen bases, are effective foam suppressors and are useful in many embodiments of our invention. Likewise, as stated ante, the addition salts of these amines with dioctyl phosphate and other acid octyl phosphate esters are also effective anti-

foam agents and may be employed in any of the foregoing examples to obtain improved oil compositions resistant to foaming.

Thus, in the general practice of our invention, a wide variety of organic ammonium octyl phosphate salts, within the broad class defined herein, may be employed to prevent or suppress the foaming of mineral oils and oil compositions. As a class, our new anti-foam agents are readily soluble in mineral oils and lubricants and are excellent foam suppressors. Their use in mineral lubricating oils and compounded lubricants has been fully illustrated ante.

While our invention has been described above with reference to specific examples and embodiments, it will be understood that the invention is not limited to such illustrative examples and embodiments but may be variously practiced within the scope of the claims herein made.

20 What we claim is:

1. A mineral oil composition resistant to foaming, comprising mineral oil and a small proportion of nicotine isoamyl octyl phosphate, the proportion of nicotine isoamyl octyl phosphate being sufficient to overcome the normal foaming tendency of the mineral oil and to suppress the foaming of the oil composition when agitated under service conditions.

2. As an improvement in suppressing the foaming of mineral oils and oil compositions when agitated in the presence of air and other gases, the improvement which comprises maintaining from 0.01 to 1.0 per cent by weight of nicotine isoamyl octyl phosphate dissolved in the oil while being so agitated, the amount of nicotine isoamyl octyl phosphate being sufficient to suppress foaming of the oil composition during such agitation.

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