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DRIER METAL SALT AND PROCESS OF
MAKING IT

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Our invention relates to new water insoluble polyvalent metal salt compounds and to processes for manufacturing the same. More particularly, our invention relates to water insoluble polyvalent metal salt compounds and compositions which are suitable as siccatives for use with drying oil preparations, lacquers and varnishes, as bodying agents for lubricating oils or greases and as fungicides for admixture to paints or for the impregnation of cloth.

One object of our invention is to produce water insoluble polyvalent metal salt compounds which are soluble to a considerable concentration in drying oil preparations, petroleum distillates, turpentine and other organic solvents and which form with such solvents highly stable solutions free from turbidity or sediment.

Another object of our invention is to provide salt compounds of the type specified which in suitably diluted solutions do not noticeably affect the color of the paint or varnish or, in the case of their use as textile impregnants, of the cloth to which they are applied.

Still another object of our invention is to produce polyvalent metal salt compounds and compositions which are capable of being stored for extended periods without being subject to deterioration.

A further object of our invention is to provide polyvalent metal salt compounds soluble in organic solvents which are substantially free of objectionable odors.

A still further object of our invention is to manufacture polyvalent metal salt compounds which are soluble in organic solvents and in oils and which do not precipitate from their oil solutions on long standing, even when the oil is chilled.

According to the present invention, we accomplish these and other objects to appear more clearly as the specification proceeds, by means of a series of new compounds which may be generically classified as the polyvalent metal salts of the acid phosphoric acid esters containing at least 5 aliphatically arranged carbon atoms.

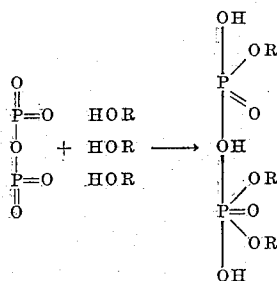
The new compounds according to our invention are obtained by reacting a compound selected from the group consisting of the acid phosphoric acid esters containing at least 5 aliphatically arranged carbon atoms and their water soluble salts

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with a polyvalent metal compound selected from the group consisting of the oxides, hydroxides, carbonates and the water soluble salts of the polyvalent metals.

The term "polyvalent metals," as used herein, includes the common divalent and trivalent metals, and, particularly, the so-called "polyvalent drier metals," i. e. lead, manganese, zinc and cobalt, the salts of which are the most important agents for the purpose of accelerating the drying of autooxidizable oils, paints, varnishes, plastic masses containing drying oils and similar resinous coating materials. The salts of other polyvalent metals such as aluminum, calcium, cerium, copper, iron, vanadium, mercury, chromium, nickel etc. are less efficient as siccatives, but some of the alkyl phosphate salts of these latter metals were found to have valuable germicidal or fungicidal properties. Other metal salts of this type are useful as bodying agents for lubricating oils or greases, as hardening agents in oleoresinous varnishes or as resins, and the present invention is intended to include and to cover all these metals, since any of them may be used to prepare the polyvalent metal alkyl phosphates according to the invention.

The acid phosphoric acid esters used in preparing the new compounds according to our invention may be obtained, for instance, by reacting 3 mols of alcohol with one mol of phosphoric anhydride according to the following general equation:



As will be seen, the product of this reaction is a mixture of primary and secondary esters. By changing the proportions of the reagents and the conditions under which the reaction is carried out, it is possible to produce greater or smaller proportions of primary and secondary

orthophosphates, respectively. If desired, pyrophosphates can be obtained instead of orthophosphates.

The alcohols used in preparing the acid alkyl phosphates forming one of the starting materials for the products, and processes of our invention may be primary or secondary, saturated or unsaturated, straight chain or branch chain alcohols having preferably more than 4 carbon atoms in the molecule. Suitable alcohols are for instance: butyl alcohol, amyl alcohol, iso-amyl alcohol, n-hexyl alcohol, lauryl alcohol, capryl alcohol, oleyl alcohol, stearyl alcohol, 2-ethyl butyl alcohol, 2,4 dimethyl n-hexyl alcohol, 1 methyl n-heptyl alcohol, 4 methyl-heptyl alcohol, etc. Mixtures of several alcohols may also be used in the preparation of the esters.

Generally, the methods for producing the acid alkyl phosphates are well known in the art as are the methods for separating the primary from the secondary alkyl phosphates, if desired, and these methods do not form part of the present invention.

The polyvalent metal salt compounds according to our invention may be prepared from primary or from secondary alkyl phosphates, or mixtures of primary and secondary alkyl phosphates may be used.

On the whole, the degree of solubility of the polyvalent metal salts of the acid alkyl phosphates in oils and in varnish thinners, such as turpentine or ligroin, depends largely upon the number of carbon atoms which are present in the alcohol radicals of the ester. The total number of carbon atoms in the alcohol radicals of the alkyl phosphates according to the invention must be at least 5, but, in order to obtain a satisfactory solubility of the polyvalent metal salts in organic solvents, the polyvalent metal phosphates containing a single alkyl group should have at least 5 carbon atoms in the alcohol radical, while the polyvalent metal phosphates containing more than one alkyl group should have at least 4 carbon atoms in each alcohol radical.

The solubility in petroleum thinners and the like of polyvalent metal salts according to the invention, which have been prepared exclusively from primary alkyl phosphates, is sometimes not entirely satisfactory, but can be greatly improved if the phosphate salts are prepared in the presence of between about 3% and about 15% (calculated on the weight of the polyvalent metal mono-alkyl phosphate) of a free aromatic or unsaturated fatty acid containing at least 6 carbon atoms, such as naphthenic acid, benzoic acid, abietic acid, linoleic acid, tung oil acid or the like. Alternatively, a small amount of such free acid may be added to the prepared salt to improve its solubility.

We found, for instance, that the manganous salt of mono n-hexyl orthophosphate is somewhat soluble in toluene and hot linseed oil and slightly soluble in naphtha. However, when this same salt is prepared in the presence of a quantity of naphthenic acid amounting to as little as 5% of the manganous n-hexyl orthophosphate, the product obtained is definitely quite soluble in naphtha and other petroleum thinners.

The effect obtained by preparing various manganous salts of mono-alkyl phosphates in the presence of a quantity of naphthenic acid amounting to 5% of the weight of the salt is illustrated in the following

Table 1

Salt	Solubility in naphtha	
	No free acid	5% naphthenic acid
Manganous salt of—		
Mono-iso-amyl orthophosphate.....	I	S
Mono-n-hexyl orthophosphate.....	SS	S
Mono-cetyl orthophosphate.....	SS	S
Mono-lauryl orthophosphate.....	PS	S
Mono-capryl orthophosphate.....	I	S
Mono-2,4 dimethyl n-hexyl orthophosphate.....	I	SG
Mono-iso-amyl pyrophosphate.....	I	S
Mono-octyl pyrophosphate.....	I	S
Mono-lauryl pyrophosphate.....	SS	S

I=insoluble.

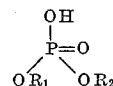
S=soluble.

SS=slightly soluble.

PS=partly soluble.

SG=forms gel-like solution.

However, we prefer to prepare our new compounds from acid alkyl phosphates or acid alkyl phosphate mixtures which consist of or contain the so-called di-alkyl orthophosphates



where R₁ and R₂ are alcohol radicals each containing at least 4 carbon atoms.

The solubility of the polyvalent metal salts of the dialkyl orthophosphates and of the mixtures containing such dialkyl orthophosphate metal salts in organic solvents increases generally with the total molecular weight of the alcohol radicals present. Thus, the manganous salt of a di-alkyl ester containing 9 carbon atoms in the alkyl radicals was found to be only slightly soluble in naphtha, but the solubility was found to increase as the manganous salts of esters containing a greater number of carbon atoms in the alkyl radicals were tested, as shown by the following

Table 2

Salt	Solubility in naphtha	Sum of C atoms in alkyl radicals
Manganous butyl amyl o-phosphate.....	SS	9
Manganous di-amyl o-phosphate.....	S	10
Manganous di-n-hexyl o-phosphate.....	S	12
Manganous di-2-ethyl butyl o-phosphate.....	S	12
Manganous i-amyl-octyl o-phosphate.....	S	13
Manganous butyl-lauryl o-phosphate.....	VS	16
Manganous butyl-oleyl o-phosphate.....	VS	22

SS=slightly soluble.

S=soluble.

VS=very soluble.

Similarly, the polyvalent metal dialkyl phosphates having two equal alkyl groups are generally less soluble in organic solvents than the corresponding polyvalent metal salts of the dialkyl phosphates having two different alcohol radicals, one thereof being equal to the alkyl groups of the salt to be compared, while the other contains a greater number of carbon atoms.

Thus, the polyvalent metal salts of iso-amyl-octyl orthophosphate were found to be generally more soluble in hot linseed oil, turpentine and

naphtha than the corresponding salts of di-amyl orthophosphate as shown by the following

Table 3

Salt	Hot linseed oil	Turpentine	Naphtha
Cobaltous di-amyl orthophosphate.	I	SS	SS
Cobaltous iso-amyl-octyl orthophosphate.	S	S	S
Manganous di-amyl orthophosphate.	SS	S	S
Manganous iso-amyl-octyl orthophosphate.	S	S	VS
Plumbous di-amyl orthophosphate.	S	S	S
Plumbous iso-amyl-octyl orthophosphate.	S	VS	VS

I=insoluble.
SS=slightly soluble.
S=soluble.
VS=very soluble.

It was further found that the presence of a fraction of a mol of a long chain alcohol radical containing more than 10 carbon atoms, such as an oleyl or stearyl radical, in alkyl phosphates containing prevalently short alkyl groups, has a considerable influence on the resulting solubility in organic solvents of the polyvalent metal salts prepared from such phosphates.

In order to test the drying properties of our new compounds, raw linseed oil was mixed with 0.5% of its weight of lead in the form of

- (1) Plumbous di-amyl orthophosphate.
- (2) Plumbous iso-amyl-octyl orthophosphate.

Panels of each were poured on glass and set aside to dry and both showed satisfactory drying properties.

In another test, a white enamel-containing 40% oil was prepared and then there was added 0.05% manganese (based on the weight of the oil) in the form of

- (1) Manganous di-amyl orthophosphate.
- (2) Manganous octyl-amyl orthophosphate.

Each enamel was painted out on a panel. The time required for these panels to dry at room temperature was as follows:

- (1) Tack-free in 27 hours.
- (2) Tack-free in 26 hours.

According to a specific embodiment of our invention improved drier compositions of the naphthenic type are prepared in the form of complex salts containing more than one acid radical. Chemically these new compounds represent probably complex metal salts in which one valence of

the polyvalent metal is bound to the alkyl orthophosphate acid radical and another valence of the metal is bound to a naphthenic acid radical. This seems to be the case since a simple mixture of the corresponding straight metal naphthenate with the straight metal salt of the acid alkyl phosphate was found to have a solubility in naphtha or linseed oil different from and less than that of the complex salt made from the same acids.

The complex polyvalent metal naphthenates of the monoacid di-alkyl orthophosphates may be prepared by themselves or in a mixture containing between 20% and 60% of the corresponding polyvalent metal binaphthenate.

The naphthenic acids used in preparing the new complex salts and salt mixtures according to our invention are the commercial grades of the kind obtained from Californian, Russian, Rumanian or other naphthenic petroleum, and should have, preferably, an acid number between about 250 and 315.

The siccative metal salts and salt mixture consisting of or containing the polyvalent metal naphthenates of monoacid di-alkyl orthophosphates, differ from the straight naphthenates not only in their chemical constitution but also in their physical properties. They are for example much more soluble in raw linseed oil at low temperatures than the corresponding straight metal naphthenates. Furthermore, for instance, the new complex manganous salts and salt mixtures have a pale straw color instead of the characteristic red or dark brown color of the manganese naphthenates which have been known heretofore.

The tendency of the simple polyvalent metal naphthenates to precipitate from linseed oil is well known in the art, and this precipitation is particularly prominent at lower temperatures.

Our complex polyvalent metal naphthenates of the monoacid di-alkyl phosphates and their mixtures with polyvalent metal binaphthenates are much less inclined to precipitation and our straight polyvalent metal salts of monoacid dialkyl phosphates are almost entirely free of any tendency to precipitate.

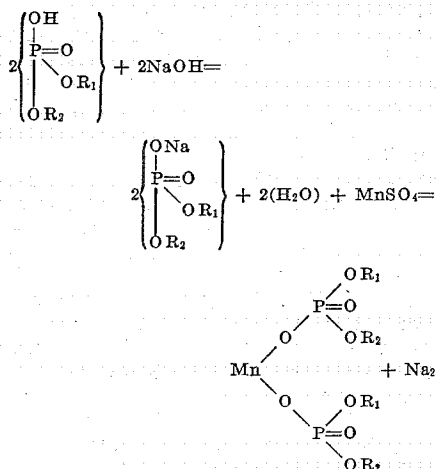
For instance, 1% solutions in naphtha (expressed as metal content) of lead naphthenate and of several complex and simple lead alkyl phosphates were added to raw linseed oil in a proportion to give a 0.5% lead content calculated on the weight of the oil. The oil and drier mixtures were then placed in a refrigerator at 13° C. The results are shown in the following

Table 4

Salt	Appearance of oil after chilling to 13° C. for—	
	24 hours	96 hours
Pb-binaphthenate.	Heavy precipitation.	Very heavy precipitation.
di-amyl orthophosphate.	Slight precipitation.	Heavy precipitation.
Pb naphthenate 4 mol i-amyl-octyl orthophosphate.	Oil almost clear.	Fairly heavy precipitation
Pb naphthenate 6 mol Pb-binaphthenate i-amyl-octyl orthophosphate.	Oil perfectly clear.	Some precipitation.
Pb naphthenate Pb-di-amyl-orthophosphate.	do.	Very slight precipitation.
Pb-i-amyl-octyl orthophosphate.	do.	Oil perfectly clear.

Several methods were found suitable for the production of our new polyvalent metal alkyl phosphates and their mixtures.

According to one (cold reaction) method, an acid alkyl phosphate having at least 5 carbon atoms is first neutralized by means of an alkali metal hydroxide, acetate or carbonate, and the resulting water soluble salt is reacted in an aqueous medium with a water soluble salt, such as the acetate, chloride or sulfate of the selected polyvalent metal. The water insoluble metal alkyl phosphate is formed by double decomposition as illustrated for instance by the following equation:



The water insoluble polyvalent metal alkyl phosphate is then separated from the aqueous medium which latter retains dissolved therein the alkali metal acetate, chloride or sulfate.

In one modification of the process described, the reaction is effected in an agitated mixture of water and an organic solvent, such as for instance naphtha, ligroin, toluene or the like. After completion of the reaction, the mixture is placed in a separatory funnel or is allowed to stand until two layers are formed which are separated from each other by decanting, drawing off of one layer, or the like. The organic solvent layer contains dissolved therein the polyvalent metal alkyl phosphate. Alternatively, the mixture may be centrifuged to separate the water solution of the alkali metal salt from the organic solvent solution of the phosphate. In all these cases the dry polyvalent metal alkyl phosphate may be obtained from its solution by evaporation of the solvent.

If no organic solvent is added to the aqueous reaction medium, the polyvalent metal alkyl phosphate forms a precipitate which can be filtered off or separated in any desired manner from the aqueous solution of the alkali metal salt. The precipitate may be washed and dried to yield the metal alkyl phosphates in the form of powders or more or less coherent solids.

According to another (hot reaction) method, an acid alkyl phosphate of the type set forth is heated to a temperature above 120° C. in the presence of an oxide, hydroxide, acetate or carbonate of a polyvalent metal until the polyvalent metal alkyl phosphate has been formed and the byproducts of the reaction, such as water, acetic acid or carbon dioxide, have been evaporated.

The hot reaction may be effected in the presence of a high boiling solvent, such as kerosene, mesitylene or xylene, in which the reaction product remains dissolved. Alternatively, the acid

alkyl phosphate and the polyvalent metal compound may be fused together in the absence of any solvent.

The cold reaction, as well as the hot reaction, may be carried out in the presence of an aromatic or an unsaturated fatty acid having more than 6 carbon atoms in the molecule, such as for instance naphthenic acid, benzoic acid, abietic acid, linoleic acid, tung oil fatty acid and the like, or such acids may be added to the finished product to increase its solubility.

If the polyvalent metal salts to be produced are those of a diacid alkyl phosphate, the quantity of free acid added is preferably between 6% and 20% by weight of the diacid alkyl phosphate. However, if polyvalent metal naphthenates of monoacid dialkyl orthophosphates are to be manufactured, it is desirable to add from about 50% to about 230% by weight of the acid alkyl phosphate, preferably in the form of naphthenic acid or its salts.

The following examples may serve to illustrate, without limiting, our invention:

Example 1

21 g. (0.1 mol) of mono 2,4 dimethyl n-hexyl diacid orthophosphate are mixed with 40 g. (0.2 mol) of a 20% sodium hydroxide solution and the mixture is diluted with 100 cc. of water. 28 g. of naphtha are stirred into the solution, followed under constant stirring by 100 g. (0.1 mol) of a 25% aqueous cobaltous acetate solution and 1.3 g. of naphthenic acid. The mixture is placed in a separatory funnel where it forms, upon standing, two layers. The top layer is decanted and washed with water until it assumes a bluish-purple color. The product obtained is a slightly acid solution in naphtha of the normal cobaltous salt of mono-2,4-dimethyl n-hexyl orthophosphate having a metal content of about 10% calculated on the weight of the solution and of about 20% calculated on the weight of all the solids. It is useful as a drier for drying oil paints, varnishes and the like.

Example 2

16.8 g. (0.1 mol) of mono-iso-amyl diacid orthophosphate are stirred into 100 g. of an aqueous solution containing 27.2 g. (0.2 mol) of sodium acetate in 72.8 cc. of water. Then, 136 g. (0.1 mol) of a 20% aqueous mercuric chloride solution are gradually added, and the mixture is stirred until no further precipitation occurs. The precipitate is filtered off, washed with water and dried. 36.7 g. of the normal mercuric salt of mono-iso-amyl orthophosphate are obtained in the form of a yellowish powder. 4 g. of abietic acid are added to and thoroughly mixed with the phosphate. The resulting product is soluble in organic solvents and useful as a germicide or fungicide.

Example 3

173 g. (0.5 mol) of mono-lauryl pyrophosphate are dissolved in 400 g. kerosene. The solution is heated to 150° C. and 39 g. (0.5 mol) of aluminum hydroxide are added under stirring. The mixture is kept at about 150° C. and is continuously agitated until, after about one hour, the aluminum hydroxide has completely reacted with the phosphate and the water of reaction has evaporated. The residue is cooled and consists of a stable solution in kerosene of the aluminum salt of mono-lauryl pyrophosphate.

Example 4

72.5 g. (0.25 mol) of mono-octyl pyrophosphate are mixed with 14 g. (0.05 mol) of linoleic acid and the mixture is fused in an open vessel at about 200° C. with 87.8 g. (0.4 mol) of zinc acetate until, after about 1½ hours, the water and the acetic acid formed in the reaction have been completely evaporated. The resulting fused mass is soluble in organic solvents and consists of about 96 g. of the zinc salt of mono-octyl pyrophosphate in mixture with about 15.5 g. of zinc linoleate. The product is useful as a drier. It contains about 23.5% by weight of metal.

Example 5

220 g. (2.5 mol) of amyl alcohol and 133 g. (0.5 mol) of an alcohol mixture containing approximately equal parts of oleyl alcohol and stearyl alcohol are reacted in a closed vessel with 142 g. (1 mol) of phosphoric anhydride. The resulting product is probably a mixture of a primary and several secondary orthophosphoric acid esters.

100 g. (0.4 mol) of this mixture are neutralized with 415 g. (0.3 mol) of a 10% potassium carbonate solution in water. Then, 227 g. (0.3 mol) of a 20% aqueous solution of anhydrous manganous sulfate are gradually stirred into the clear solution until no further precipitation is obtained. The precipitate is filtered off, washed twice with water and heated to drive off moisture. The residue is a brownish waxy solid which is completely soluble in naphtha and, even in highly concentrated solutions, does not seem to have any tendency to gel. For instance, a 40% solution of the resulting salt mixture in naphtha does not form a gel upon standing. The product contains about 14% by weight of metal and may be incorporated into an autooxidizable drying oil composition to accelerate its rate of drying.

Example 6

23.8 g. (0.1 mol) of di-amyl orthophosphate are mixed with 50 g. of turpentine and 11.2 g. (0.1 mol) of a 50% solution of potassium hydroxide in water are added. The mixture is stirred and 47.6 g. of an aqueous solution containing 11.9 g. (0.05 mol) of nickelous chloride are run in. A precipitate is formed which, when heated and stirred, readily dissolves into the turpentine. The mixture is centrifuged to remove the water and a solution of nickel-di-amyl phosphate in turpentine is obtained. The product can be used as bodying agent for lubricating oils.

Example 7

28 g. (0.1 mol) of octyl amyl orthophosphate are mixed with 50 g. of ligroin and 8 g. (0.1 mol) of a 50% sodium hydroxide solution in water and slowly stirred into the resulting solution. 44.6 g. (0.05 mol) of a 25% aqueous solution of tetrahydrate manganous sulfate are run in. The resulting precipitate dissolves readily in the ligroin upon stirring. Thereafter, the mixture is left to stand until it has separated into two layers. The lower layer which consists of an aqueous sodium sulfate solution in water is drawn off and the residue is a clear solution in ligroin of the normal manganous salt of octyl amyl orthophosphate.

When the solvent is evaporated, there remains a dark brown plastic-like solid which is readily soluble in naphtha, turpentine, drying oils and the like. The product contains 9% of metal and

has a pronounced accelerating effect on the rate of drying of drying oil compositions to which it is added. The color of a 1% solution in naphtha of manganous octyl amyl phosphate is considerably lighter than that of a corresponding solution of manganous naphthenate.

Example 8

306 g. (3 mol) of 2-ethyl butyl alcohol are reacted in a closed vessel with 142 g. (1 mol) of phosphoric anhydride. 45 g. (0.2 mol) of the resulting mixed primary and secondary 2-ethyl butyl orthophosphate are neutralized with 60 g. (0.3 mol) of a 20% sodium hydroxide solution. The mixture is placed in a separatory funnel. 100 g. of naphtha are added and the whole is well mixed. 150 g. (0.15 mol) of a 25% aqueous cupric sulfate solution are introduced in portions of 15 g. each, shaking well after each addition until no further precipitation is observed and the precipitate formed has disappeared. The mixture is allowed to separate, and the top layer containing the copper salt of 2-ethyl butyl orthophosphate is drawn off and washed well. The product is a clear dark green solution which is particularly suitable as an impregnant for cloth to prevent mildewing.

Example 9

149 g. (0.5 mol) of butyl lauryl monoacid orthophosphate are fused in a heat resistant open reaction vessel at a temperature of about 320° C. with 149 g. (0.25 mol) of plumbous carbonate, until the reaction is completed and the water of reaction has completely evaporated. The resulting fused mass is soluble in drying oils and other organic solvents, has good drying properties and contains about 25% by weight of lead.

Example 10

124.5 g. (0.3 mol) of amyl-oleyl monoacid orthophosphate are dissolved in 200 g. mesitylene. The solution is heated to 160° C. and 7.6 g. (0.05 mol) of chromic oxide are slowly added under stirring. The mixture is kept at 160° C. and is agitated for about 1 hour, i. e. until the reaction has been completed and the water of reaction has been evaporated. The residue is a solution in mesitylene of the chromic salt of lauryl oleyl orthophosphate containing about 39% solids, with a metal content of about 4% by weight of the solids. The product is suitable as a bodying agent for lubricating oils.

Example 11

9.5 g. (0.04 mol) of di-amyl monoacid orthophosphate are mixed with 20.5 g. (0.16 mol) of naphthenic acid. 40 g. (0.2 mol) of a 20% aqueous sodium hydroxide solution are added under stirring to neutralize the acid groups. The reaction product is mixed with 50 g. toluene and 60 g. of a manganous sulfate solution containing about 25% (15.1 g.=0.1 mol) of anhydrous manganous sulfate. A precipitate is formed which upon stirring goes into solution with the toluene. The mixture is left standing until two layers are formed. The top layer is decanted and washed and consists of a solution in toluene of the normal manganous naphthenate of di-amyl orthophosphate in mixture with an approximately equal weight quantity of normal manganous binaphthenate. The total weight of the solids in the solution is 35.3 g. or 41% and its metal content is 5.5 g.=15.6% of the solids. The product is soluble in drying oils of all types and acts as an efficient siccative on such oils.

Example 12

14 g. (0.05 mol. of octyl-amyl monacid orthophosphate are mixed with 13 g. (0.1 mol) of naphthenic acid. The mixture is neutralized with 60 g. of a 10% sodium hydroxide solution in water containing 0.15 mol of sodium hydroxide. Then, 105 g. (0.075 mol) of a 20% aqueous cobaltous sulfate solution are added and the mixture is stirred until no further precipitate is formed. The water is decanted and the residue, after washing and drying, consists of a mixture of about 3 parts by weight of the cobaltous naphthenate of octyl-amyl orthophosphate with about 1 part by weight of cobaltous binaphthenate. The mixture is easily soluble in most organic solvents and in drying oils and forms highly stable solutions with the latter. It has, in small percentage quantities, a marked accelerating effect on the rate of drying of such oils, and, if added in practical proportions, it does not cause any discoloration of the drying oils or of coating compositions containing the drying oils. The metal content of the salt mixture is about 4.5 g.=15% of the solids.

Example 13

19 g. (0.08 mol) di-amyl monoacid orthophosphate and 10.3 g. (0.08 mol) naphthenic acid are fused in an open vessel for about 30 minutes at 150° C. with 19.3 g. (0.08 mol) of lead hydroxide.

The resulting brown waxy plastic, which is the complex lead naphthenate of di-amyl orthophosphate, can be dissolved in naphtha and is an efficient siccative for drying oils. It contains about 37% of lead.

Example 14

56 g. (0.2 mol) of octyl amyl monacid orthophosphate and 128 g. (1 mol) of naphthenic acid are dissolved in 200 g. of xylene. The solution is heated to 140° C. and 133.8 g. (0.6 mol) of litharge are slowly added under stirring. The mixture is kept at 140° C. and is agitated for about 1½ hours. The reaction product goes into solution in the xylene while the water of reaction is evaporated. When the reaction is completed the residue is cooled. The product is a solution in xylene of a salt mixture consisting probably to about 2/5 of its weight of the complex lead naphthenate of octyl amyl orthophosphate and to about 3/5 of its weight of lead binaphthenate. The solid contents of the solution are about 60% by weight and its metal content amounts to about 40% of the total weight of the solids.

The solution can be mixed with drying oils and drying oil compositions to accelerate their rate of drying. It is free of objectionable odors and, in the proper dilution, does not cause any dis-

coloration of the drying oil compositions to which it is added.

We claim:

1. As a new product, a complex salt of naphthenic acid and a dialkyl, monoacid orthophosphate having at least four carbon atoms in each alkyl radical with a polyvalent metal selected from the group consisting of lead, manganese, zinc and cobalt.
2. As a new product, a complex salt of naphthenic acid and a dialkyl, monoacid orthophosphate having two different alkyl radicals each containing at least four carbon atoms with a polyvalent metal salt selected from the group consisting of lead, manganese, zinc and cobalt.
3. As a new drier for paints and varnishes, the complex lead naphthenate of octyl-amyl orthophosphate.
4. A method for producing new polyvalent metal salts comprising the steps of heating a monoacid dialkyl orthophosphate containing at least 4 carbon atoms in each alkyl radical with a compound selected from the group consisting of oxides, hydroxides, carbonates and acetates of the polyvalent drier metals in the presence of a quantity of naphthenic acid amounting to 50% to 230% by weight of the acid dialkyl phosphate to a temperature above 120° C. until the complex polyvalent metal naphthenate of the secondary alkyl phosphate has been formed.
5. A method for producing new polyvalent metal salts comprising the steps of dissolving 100 parts by weight of a monoacid dialkyl orthophosphate containing at least 4 carbon atoms in each alkyl radical and between 50 and 230 parts by weight of naphthenic acid in a high boiling solvent, heating the solution to a temperature slightly below the boiling point of the solvent, adding to the hot solution a quantity of a compound selected from the group consisting of the oxides, hydroxides, carbonates and acetates of the polyvalent drier metals, stirring the mixture until the reaction has been completed, and recovering the organic solvent containing dissolved therein the complex polyvalent metal naphthenate of the secondary alkyl phosphate.
6. A method for producing a polyvalent metal salt which is soluble in organic solvents and suitable as a drier for paints and varnishes, said method comprising the steps of dissolving 56 parts by weight of octyl amyl mono-acid orthophosphate and 128 parts by weight of naphthenic acid in 200 parts by weight of xylene, heating the solution to about 140° C. stirring 133.8 parts by weight of litharge into the hot solution until the reaction has been completed, and cooling the resulting solution.

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