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PHOSPHATE ESTERS

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No Drawing. Application December 30, 1935,
Serial No. 56,724

22 Claims. (Cl. 260—403)

My invention relates to a new class of chemical substances and is a continuation in part of my prior application, Serial No. 705,825, filed January 8, 1934, now Patent No. 2,026,785, and it also contains subject matter present in my prior application, Serial No. 14,528, filed April 3, 1935.

My invention relates more in particular to a new class of chemical substances, specifically esters of phosphoric acids and substances containing phosphorus and capable of forming esters of phosphoric acids, having the properties of interface modifiers and adapted for use in many industries.

In another co-pending application, Serial No. 710,893, filed February 12, 1934, I describe the use of my improved esters of phosphoric acids of the character described in my prior application, Serial No. 705,825, now Patent No. 2,026,785, of which this a continuation-in-part, for use as viscosity reducers and improvers generally of certain types of confections, such as chocolate mixes for coatings and the like. I have now found that I can improve the potency of the products of my invention as ingredients of confections, and also enhance their value generally as interface modifying agents for other purposes and in other industries.

The object of my present invention is the provision of a new class of chemical substances.

Another object is the provision of a class of chemical substances adapted for use as interface modifiers.

Still another object is to improve the potency and other characteristics of the modifying agents described in my prior application, Serial No. 705,825, now Patent No. 2,026,785, of which the present application is a continuation-in-part.

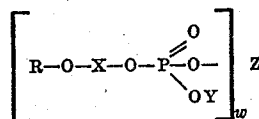
Other objects and features of the invention will be apparent from the following description.

Although my present invention relates in general to an improvement in the process of producing esters of phosphoric acids of the type described in my prior applications, I shall describe in the present application a manner of making the esters of phosphoric acids with or without my improved treatment. Generally this improvement consists in a pretreatment step, the character of which will be described more in detail hereinafter, prior to the actual esterification with phosphoric acids or substances containing phosphorus and being capable of forming esters of phosphoric acids. By means of this pretreatment step the character of the final product is modified radically in many of its properties and improved results are secured in the industries in

which frothing, wetting, penetrating, detergent, emulsifying, and other interface modifying functions are desired.

In general, the esters of phosphoric acids of my invention are possessed of at least two groups, one having a hydrophile function and the other having a lipophile function in the molecule. The hydrophile function is performed primarily by a hydrophile phosphate group, that is, a group containing phosphorus in the form of a phosphorus oxide acid radical, which gives to the molecule as a whole an affinity for aqueous materials. The lipophile portion of the molecule contains at least one lipophile group, that is, a group or radical having a definite affinity for oil and fats. The lipophile radical may be of acyl or alkyl character and may be derived from a fatty acid or a corresponding alcohol. For achieving the most satisfactory results for the purposes which have been set forth herein, the lipophile radical should contain a minimum of six carbon atoms, and, preferably, should contain the higher carbon compounds, particularly those having from twelve to eighteen carbons. The hydrophile phosphate group is linked to the lipophile group by means of a polyhydroxy substance, such as sugars, sugar alcohols, glycols, glycerol, polyglycols, polyglycerols, polyhydroxycarboxylic acids of the mono- and poly-basic classes, oxidation products of polyhydroxy substances such as glyceric acid, etc., the nature of which polyhydroxy substance will be referred to more in detail hereinafter. The linkage between the polyhydroxy substance and the lipophile group may be either an ester or an ether linkage.

Many of the compounds of my invention may be represented by the formula



wherein "R" is a lipophile group, "X" is the residue of a polyhydroxy substance, "Y" and "Z" are cations, and "w" is a small whole number.

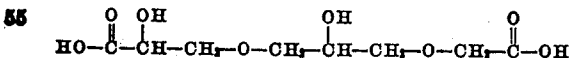
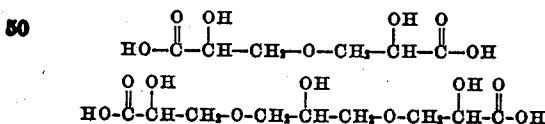
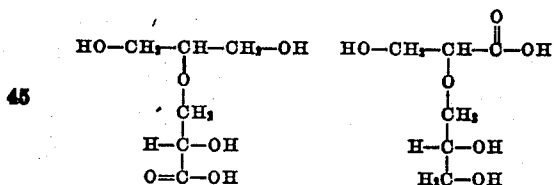
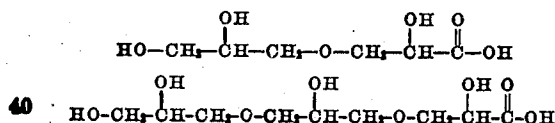
More specifically, the compounds of my invention may be defined as phosphoric acid esters of polyhydroxy substances wherein at least one hydroxy group of the polyhydroxy substance has its hydrogen substituted by a lipophile group. Preferably, particularly for use in foods, the compounds are devoid of groupings wherein nitrogen is linked directly to carbon belonging to radicals in esterified form, as, for example, in choline groups, but by this expression I do not mean to

exclude compounds with inorganic ammonium nitrogen and compounds containing nitrogen linked to carbon belonging to cationic, i. e., salt forming radicals which are not in esterified form.

Wherever the term "non-nitrogenous" is hereinafter employed, it will be understood to have this significance.

The lipophile group may include any fatty acid group or relatively high molecular weight organic carboxylic acid group such as the acid radicals of the following acids: caproic, caprylic, capric, hydroxystearic, benzoic, benzoylbenzoic, naphthoic, toluic, hydroxybenzoic, palmitic acid, stearic, lauric, melissic, oleic, myristic, ricinoleic, linoleic acid or mixed fatty acids derived from animal or vegetable sources, for example, lard, coconut oil, corn oil, cottonseed oil, sardine oil, partially or completely hydrogenated animal and vegetable oils such as cottonseed oil, corn oil, lard, sesame oil and fatty acids of various waxes such as beeswax, spermaceti and carnauba wax or hydroaromatic acids such as abietic acid, etc., or the lipophile group may be an alkyl radical derived from an alcohol corresponding to any of the preceding acids, such as cetyl alcohol, lauryl alcohol, oleyl alcohol, dodecenol, etc.

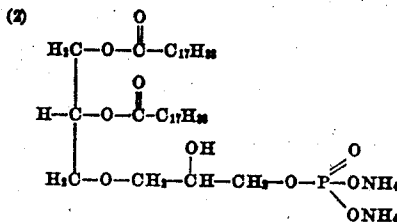
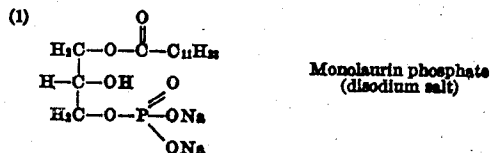
Specific examples of polyhydroxy substances, the residues of which may serve as linkages between the lipophile groups and the hydrophile phosphate groups are as follows; mucic acid, tartaric acid, saccharic acid, gluconic acid, glucuronic acid, gluconic acid, mannonic acid, trihydroxyglutaric acid, glyceric acid, and the like, as well as carboxylic oxidation products of polyglycerols which may be represented by the formulae:



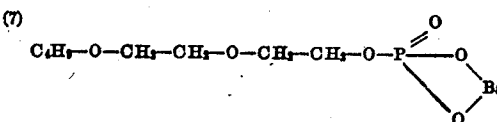
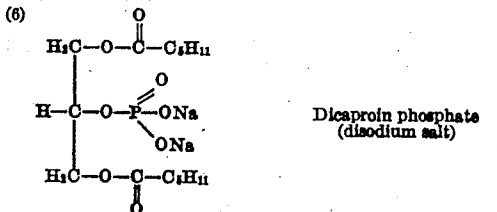
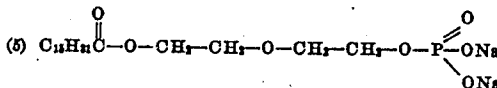
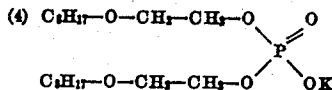
and sugars such as: xylose, galactose, fructose, maltose, glucose; sorbitol, dulcitol, arabitol and other sugar alcohols such as hexahydric alcohols derived from sugars, and other substances having free hydroxy groups; glycerol, polyglycerols, glycols, polyglycols. The above polyglycerols and their oxidation products are produced by polymerizing glycerine, preferably by heating with about 1% of alkali at temperatures from 250° to 260° C. for about three hours in the presence of an inert gas. This reaction mixture will give a mixture of various polyglycerols, the size of the molecules depending upon various factors such as the time of polymerization, etc. The mixtures of polyglycerols are then oxidized with mild oxidizing agents such as hot dilute nitric acid, permanganates, bromine water, etc., to convert at least one of the primary hydroxy groups to a

carboxylic group. Preferably, however, the oxidation treatment is applied to the polyglycerol esters or ethers containing free hydroxy groups.

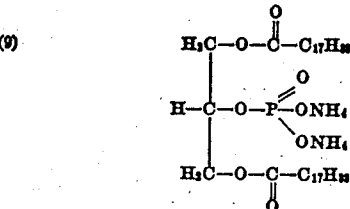
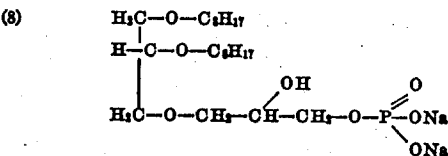
Examples of substances of my invention may be represented as follows:



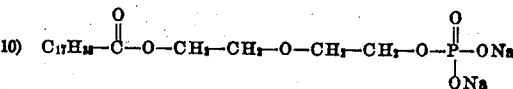
(3) Cetyl sorbitol phosphate



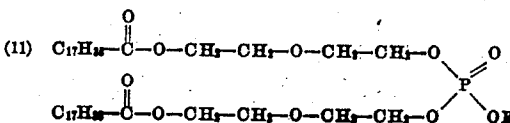
Butyl ether of diethyleneglycol phosphate (barium salt)

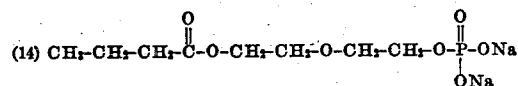
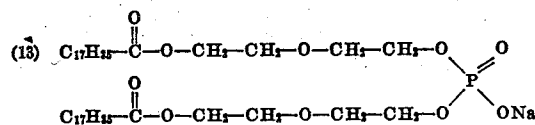
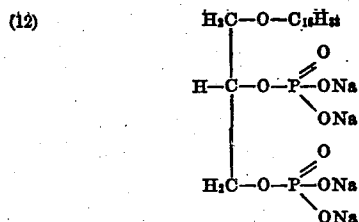


Diolein phosphate (ammonium salt)



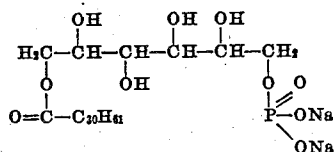
Stearic acid ester of diethylene glycol disodium orthophosphate





(15) Sorbitol stearate monophosphate (ammonium salt)

(16) Sorbitol melissate monophosphate (sodium salt):



There are several methods by means of which the materials of my invention may be made. The method employed should be determined primarily by considering the type of substance to be produced. In introducing the phosphate radical, for example, a material containing an esterifiable hydroxy group is reacted with phosphorus pentoxide, pyrophosphoric acid, meta-phosphoric acid, phosphorus halides, ethyl metaphosphate, phosphorus trioxide, phosphorus pentachloride, phosphorus oxychloride or some other reagent capable of furnishing the elements required for the formation of a phosphorus acid. Either one or more phosphate radicals may be introduced, depending upon the substance desired. A condensing agent and/or a solvent may be added where required.

An important feature of my invention is the pre-treatment step prior to actual esterification of the hydroxy group or groups to form the phosphoric acid ester. This pretreatment comprises treating the higher fatty acid or similar ester or ether of the polyhydroxy substance with an agent capable of furnishing the elements of a phosphorus acid, this pretreatment being preferably carried on at a somewhat higher temperature than the temperature at which the final esterification takes place. In general, I have found that the most suitable agent for pretreatment is phosphorus pentoxide. Preferably the pretreating agent is removed from the reaction product after the preliminary treatment or pretreatment by suitable means such as filtering, centrifuging, or the like, but marked improvement results even though the pretreating agent is not removed before the final esterification step. For the convenience of those skilled in the art, I shall first describe the conventional manner of carrying out the esterification step without reference to the pretreatment and shall then describe the manner in which the pretreatment is employed in the examples given.

Example A.—As a specific example, 7 parts of glycerol monostearate (monostearine) are dissolved in 35 parts of dry pyridine. To this solution are added, with simultaneous cooling, 12

parts of phosphorus oxychloride dissolved in 50 parts of dry acetone, the mixture being stirred meanwhile. This mixture is allowed to stand over night and it is then thrown into 300 parts of water with stirring. A precipitate forms at first, but after a few moments this becomes completely dispersed. On warming to about 60° C., the solution becomes highly colored. 15% of salt is now added to throw the product out in the form of a precipitate. This precipitate contains approximately 73% of moisture after the greater proportion of salt solution has been separated therefrom. The product may be used in this form or it may be further washed or otherwise purified. It may be dried or not, as desired. The product so formed is primarily a glycerine ester in which one hydroxy group is esterified with a stearic acid radical and at least one other hydroxy group is esterified with phosphoric acid. The monolauric acid ester of glycerine phosphate may be prepared in a similar manner, but using substantially pure lauric acid, or the fatty acids of coconut oil containing about 40% lauric acid in preparing the monoglycerides which are to be subsequently reacted with phosphorus oxychloride. The resultant product is neutralized with sodium bicarbonate to produce the sodium salt. This procedure for the preparation of phosphoric esters is a convenient method for making certain materials of my invention which are represented by Nos. 3, 4, 6, 7, 11 and 13 in the list of examples shown hereinabove, as well as others, bearing in mind that particularly where secondary phosphates are concerned (such as Nos. 4, 11, 13 in the list of examples shown hereinabove) the phosphorus oxychloride must be added gradually to the reactant with the hydroxy group, so that the latter is always present in excess throughout the course of the reaction.

Example B.—According to another example, 66 parts of monobutyl ether of diethylene glycol are mixed with 58 parts of phosphorus pentoxide. This is accomplished best by adding, with stirring, the phosphorus pentoxide gradually and in small portions to the monobutyl ether of diethylene glycol and cooling somewhat, if necessary, to avoid excessive heating. This mixture is allowed to remain at room temperature for about half an hour. The mixture is then taken up with about 800 parts of cold water and 20 parts of barium chloride stirred in, the latter being in the form of a 10% aqueous solution. 125 parts of salt are now dissolved in this mixture. The entire mixture is allowed to remain at rest until the product floats to the surface, whereupon the brine is withdrawn and discarded. The product may be used in this form or it may be filtered or concentrated further or otherwise treated, as desired. The finished product, the principal portion of which may be represented by No. 7 in the list of examples shown hereinabove, is easily dispersible in water and exhibits many useful colloidal properties, particularly as an interface modifier.

Example C.—As an illustration of the pretreatment step I shall refer to the illustrative embodiment given in Example A. In the pretreatment step, 700 parts of mono stearic acid ester of glycerol are first mixed in a dry condition with 75 parts of finely divided phosphorus pentoxide (P₂O₅), the temperature of the mono stearic acid ester of glycerol being raised and held at 160° F., and the mixture being thoroughly agitated during the introduction of the P₂O₅. The temperature of the mixture rises to about 200° to 210° F. The container is now heated, as,

for example, by the circulation of steam in a suitably provided jacket to raise the temperature to 240° F., and the mixture is maintained at that temperature for about one-half hour with constant agitation. The phosphorus pentoxide material is now removed, for example with a centrifuge, and it is found that portions of organic matter are removed with the phosphorus pentoxide and that the latter becomes altered in a manner which I have been unable thus far to satisfactorily determine. When separating with a centrifuge, about one hundred and fifty parts of a very viscous brown mass are removed at this step.

The clear liquid obtained from this pretreatment step is transferred back to the kettle and cooled to about 155° F. 75 pounds of finely divided phosphorus pentoxide are then added with agitation. At the same time, cold water is circulated in the jacket. The temperature rises to about 180 to 190° F. in about five to ten minutes and remains at this temperature for several minutes and then begins to cool. It is allowed to cool to about 150° F. The total time required from the time the phosphorus pentoxide is added to the time it reaches its maximum temperature and then cooled to about 150° F. is about one-half hour. This is found to give the best results when finely divided phosphorus pentoxide is used. If coarse phosphorus pentoxide is used, it is added at about 160° F. and the temperature rises slowly to 210° F. in about twenty minutes. At this point there is a tendency for the temperature to rise, but this rise is checked by circulating cool water in the jacket. The maximum temperature obtained in this way is approximately 214° to 215° F. The reaction mixture is allowed to remain at this temperature for several minutes and is then allowed to cool to about 150° F. This takes approximately another twenty minutes. A dark, reddish-brown viscous liquid is obtained.

Example D.—As a further example of a method of carrying out my invention by a process employing the pretreatment step, the following is illustrative:

Preparation of Ester: Six hundred (600) pounds of cottonseed oil hydrogenated to an iodine value of about 69 and 150 pounds of normally liquid cottonseed oil are heated together with 250 pounds of glycerine to about 200 degrees F. without stirring. Twelve (12) ounces of sodium hydroxide flakes are added and the temperature raised to 485 degrees F. and held at that temperature for two hours with stirring. A non-oxidizing atmosphere, such as CO₂, is maintained during the heating and the cooling to about 200 degrees F. On standing, glycerine separates out and is removed. Glycerine still suspended may be centrifuged out. The resulting product contains a mixture of mono- and di-glycerides of the fatty acids present in the hydrogenated cottonseed and normally liquid cottonseed oils.

Pre-Treatment With PO₅: Seven hundred (700) pounds of the ester obtained in "D" are transferred to a jacketed kettle. Seventy-five (75) pounds of finely divided P₂O₅ are added at a temperature of 160° F. with thorough agitation. The temperature rises to about 200° to 210° F. Steam is then circulated in the jacket to raise the temperature to 240° F. and the mass is maintained at that temperature for one-half hour with constant agitation. The reaction product is then centrifuged to remove the P₂O₅ and adhering organic matter (about 150 pounds of a very viscous brown mass are centrifuged out;

practically no P₂O₅ enters into chemical combination with the ester in this pre-treatment stage).

Esterification With P₂O₅: The clear liquid obtained in the pretreatment step is transferred back to the kettle and cooled to about 155° F. Seventy-five (75) pounds of finely divided P₂O₅ are then added with agitation. At the same time cold water is circulated in the jacket. The temperature rises to about 180° to 190° F. in about five to ten minutes, remains at that temperature for several minutes, and then begins to cool. It is then allowed to cool to about 150° F. The total time required from the time the P₂O₅ is added to when it reaches maximum temperature and is allowed to cool to 150° F. is about one-half hour. This is the case when fine P₂O₅ is used. If coarse P₂O₅ is used, it is added at 160° F. The temperature rises slowly to 210° F. over a period of twenty minutes. There is then a tendency for the temperature to rise suddenly. This rise is checked by circulating cold water in the jacket. The maximum temperature obtained in that way is about 214° to 215° F. and the reaction mixture remains at that temperature for several minutes. It is then allowed to cool to about 150° F. This takes another twenty minutes. A dark reddish brown viscous liquid is thus obtained.

Neutralization: One-half of the reaction product is removed and the half remaining in the kettle is cooled to 120 degrees F. Forty (40) pounds of finely divided anhydrous sodium carbonate are added at one time with continued agitation. The temperature may rise as high as 168° F. over a period of one-half hour. It should not be allowed to rise any higher. In most cases it goes up to about 160° F. It is then raised to 168° F. and kept at that temperature for about one-half hour, with continuous agitation. There is considerable effervescence, but not as copious, violent or troublesome as when the pretreatment step is not used. The product is immediately centrifuged to remove excess sodium carbonate.

In those cases where a pretreatment step is employed, for example, with P₂O₅, it appears, oddly enough, that substantially none of the P₂O₅ combines organically with the mono- or di-glyceride or similar compound, as the case may be. In the ordinary situation, tests have shown only about 0.1% to 0.2% phosphorus (calculated as P₂O₅) present in the product after the pretreatment step. However, the pretreatment step somehow or other appears to alter or condition the mono- or di-glyceride or the like so that it becomes unusually receptive for ester formation with the phosphorus containing compound. The reaction, for example, with P₂O₅, subsequent to the pretreatment step, is radically different from what it normally is without the pretreatment step, with the result that the finished product obtained thereby is distinctly more potent for viscosity reduction and is different in many other respects from the product obtained without said pretreatment step. By proceeding in this manner, considerable amounts of phosphorus can be organically combined in the molecule of the ester or the like. For example, products containing up to 28% of phosphorus, calculated as P₂O₅, have been produced, and it is this phosphorus in the form of a phosphoric acid which represents, principally, the hydrophilic group present in the product.

While all of the substances of my invention fall into the category of interface modifiers, they differ, respectively, in their suitability for specific

interfaces, they modify interfaces in various ways and to various extents, depending upon the character and relative potencies of the hydrophilic and lipophilic groups, the resultant of the two representing the interfacial function of the molecule as a whole.

For example: the butyl ether of diethylene-glycol phosphate (No. 7 of the illustrative examples given above) and diolein phosphate (No. 9 of the list of illustrative examples given above) serve well to show how the properties of my interface modifiers may vary. No. 7 is predominantly hydrophilic, practically freely soluble in water; whereas, No. 9 is predominantly lipophilic, imbibes cold water but cannot be said to disperse freely therein. The latter does, however, disperse in hot water, particularly readily in the presence of a very low concentration of electrolyte such as sodium chloride. It is well to note that the hydrophilic group in both cases is the same, but the lipophilic group in the case of No. 9 contains approximately five times as many carbons, if not more, than the lipophilic group in No. 7. No. 9 is predominantly lipophilic; No. 7 is predominantly hydrophilic, though each possesses both hydrophilic and lipophilic properties. No. 9 when touched with moist fingers appears greasy; whereas No. 7, as stated above, is practically water soluble. No. 9 promotes water-in-oil emulsions; No. 7 promotes oil-in-water emulsions. Between such two relatively extreme examples may be inserted a series of other examples in the order of diminishing hydrophilic characteristics starting with No. 7 upward and, per contra, with increasing lipophilic characteristics working up to No. 9 and beyond. Between two vicinal members of such a series, the differences may be only very slight, becoming more appreciable the further removed any two selected members of the series are from each other.

While the illustrative examples listed hereinabove represent principally single substances, it must be understood that the invention is by no means limited to single substances. Indeed, in practice, it is frequently more convenient to prepare a mixture of the substances of my invention and to use such a mixture. For example, I may prepare a mixture of diglycerides by any convenient method, such as described hereinbelow, and then introduce into each member of this mixture of diglycerides a phosphate radical by a convenient method.

Example E.—Preparation of mixture of diglyceride phosphates from corn oil.

A mixture of 880 parts of corn oil and 50 parts of glycerol is heated in a non-oxidizing atmosphere with stirring to 220° C. About 0.88 parts of flake caustic soda are then added and the temperature is raised to 250° C. with continued stirring and is maintained at 250° C. or thereabout for two hours. The reaction mass is then cooled to room temperature in an inert atmosphere. This product is essentially a mixture of diglycerides.

To 200 parts of the above product dissolved in 600 parts of isopropyl ether (free of alcohol and water) there are added 50 parts of phosphorus pentoxide and the mixture is boiled under a reflux with stirring for three hours, care being taken to keep the reaction mixture out of contact with atmospheric moisture. This reaction product is now freed of ether, preferably by distillation.

The residue is a somewhat sirupy, oily material which may be used as such, or it may be neutral-

ized with gaseous ammonia or aqueous ammonia or other alkaline agents. Also, the product may be purified or otherwise treated if desired. It consists in the main of a mixture of diglyceride phosphates, the significant, predominant constituent of which is represented essentially by No. 9 in the list of examples hereinabove.

In the above example the pretreatment step may be employed and a product obtained which, to outward appearance, is substantially the same as the product produced without the use of the pretreatment step. The product produced by the pretreatment step, however, is much more potent for many purposes in which an interface modifying function is required, particularly for the purpose of decreasing the viscosity of confections such as chocolate and similar mixtures, and for securing other advantages in such and various other products.

In place of corn oil in the above, I can use cottonseed oil, peanut oil, sesame oil, sunflower oil, neat's-foot oil, cocoanut oils, hydrogenated animal and vegetable oils including those just enumerated, lard, tallow, etc., the fish oils such as cod liver oil, and other similar triglycerides.

If, on the other hand, it is desired to prepare a single substantially pure substance analogous to the above, it is only necessary to treat pure diolein with phosphorus pentoxide as described above.

This procedure, for introducing phosphate radicals, described directly above, I have also successfully used in the preparation of materials represented by Nos. 1, 2, 5, 6, 8, 10, 12 and 14, in the list of examples shown hereinabove, as well as others. It is, of course, obviously within the skill of any qualified chemist to compute molal proportions or multiples of molal proportions of the reactants with respect to each other.

Example F.—175 parts of refined deodorized cottonseed oil are heated with 10 parts of glycerine (United States Pharmacopoeia grade) in an inert, that is, non-oxidizing atmosphere, with stirring, to about 200° C. 17 parts of flaked caustic soda are then added with stirring, then raised to about 250° C. and maintained at this temperature with continuous stirring for about two hours, and cooled to room temperature in an inert atmosphere.

45 parts of the above product, which consists essentially of a mixture of diglycerides, and 3 parts of finely divided phosphorous pentoxide are mixed at a temperature of about 50° to 60° C., and then heated with vigorous stirring in a substantially dry, inert atmosphere to about 115° to 120° C., or, if desired, somewhat higher, and maintained at this temperature for two to three hours.

The reaction mixture is then allowed to remain at rest and to cool in an inert atmosphere. A small proportion of insoluble matter settles to the bottom of the container and while the mixture is still liquid, the latter is poured off from the sediment. The decanted material may be used as such or it is further chilled until it is semi-solid and plastic, and 50% aqueous sodium hydroxide solution is added gradually, with stirring, insufficient proportion to render the product preferably substantially neutral to litmus, though the product may be left slightly acid or faintly alkaline to litmus. The amount of sodium hydroxide solution to be added is determined as follows:

A 2 gram sample of the material to be neutralized is dissolved in about 10 c. c. of neutral

ethyl ether. 15 c. c. of neutral isopropyl alcohol are added and then 150 c. c. of distilled water are stirred in. The mixture is then titrated with $\frac{1}{10}$ normal sodium hydroxide solution, using phenolphthalein as indicator. From this titration the amount of caustic soda solution required is computed.

The product obtained consists principally of esters of phosphoric acid in the form of a light colored, pasty material with valuable interface modifying properties along the lines discussed hereinabove.

The reaction with phosphorus pentoxide described herein under Example D is susceptible to considerable variation as to the proportion of phosphorus pentoxide used, the fineness thereof, the temperature, and the duration of contact between the fatty material and the phosphorus pentoxide. In general, each of these four factors stands in reciprocal relation to the other two, that is to say, other things being equal, the greater the proportion of phosphorus pentoxide, the shorter the time of contact and/or the lower the temperature of reaction required to obtain a given result. Similarly, if the phosphorus pentoxide is relatively very finely divided, the amount thereof, the time and temperature of heating may all be reduced. Or, to state another reciprocal relation, the higher the temperature of reaction, other things being equal, the coarser may be the P_2O_5 , the shorter the duration of contact and/or the lower the proportion of phosphorus pentoxide required to obtain a given result.

However, these reciprocal relations are valid only within certain reasonable limits. For example, while at temperatures below 105°C . some reaction does occur, it is very slow, so that to get appreciable interface modifying potency in the product, the time of contact would be so long and the proportion of phosphorus pentoxide required so high as to make such a procedure extremely inconvenient, in many instances.

In the other hand, the employment of temperatures substantially higher than 140°C . in general tends to reduce the potency of the product and discolor and char it, especially so when higher proportions of phosphorus pentoxide or longer times of contact are employed. The temperature factor is particularly important in relation to the phosphorus pentoxide reaction because of the fact that this reaction is decidedly exothermic. It is evident, therefore, that while considerable latitude is permissible in the proportion of phosphorus pentoxide, in the temperature range of the reaction, and in the time of contact of phosphorus pentoxide with fatty material, certain criteria as to the inter-relationship of these three factors must be observed to secure high interface modifying potencies in the product obtained.

Notwithstanding this, however, even though the reaction be subjected to considerable, even indiscriminate, variation in the three factors indicated, the products obtained will still possess interface modifying properties such as those described herein. To be sure, in order to obtain high or outstanding potency with respect to such interface modifying properties, those skilled in the art will appreciate the importance of carefully adjusting the conditions of the reaction, particularly with respect to the three factors designated. An illustration of such preferred conditions is carefully specified hereinabove in Example D. In all cases, however, the products obtained comprise esters of phosphoric acid interfacially active in fatty compositions falling into

the class with which the present invention deals and the determinants of which are referred to at various points of this specification.

Example G.—Cocoa butter is treated by the same procedure, with the same proportions successively of glycerine and phosphorus pentoxide and other materials, and under the same conditions of time, temperatures and stirring as described in Example F hereinabove. The product obtained consists primarily of esters of phosphoric acid, somewhat firmer in texture and darker in color than the product obtained in Example F, but has substantially the same interface modifying properties.

In Example F or Example G given above, larger percentages of phosphorus pentoxide may be used, such as 25% on the basis of the glyceride and a very good, potent product will be obtained under the conditions specified. On the other hand, as low as 1% of phosphorus pentoxide may be used to react, but higher temperatures will be necessary in order to obtain a product of some potency.

In neutralizing the ester with the sodium hydroxide solution, the resultant product will contain small amounts of moisture, from about 2% to 5%, depending upon the amount of moisture introduced by the solution of the alkali.

Example H.—100 parts of oleic acid (commercially pure) of good color, odor and taste, are heated with 100 parts of glycerine (U. S. Pharmacopoeia grade) to 220°C . with stirring in an inert, that is, non-oxidizing, atmosphere, and the mixture is maintained at this temperature with continuous stirring, in an inert atmosphere, for approximately two hours, until the free fatty acid content of the oil is about $\frac{1}{2}\%$ or less. The mixture is now allowed to remain at rest and to cool in an inert atmosphere and the excess of glycerine is drawn off from the supernatant layer.

71 parts of the supernatant layer and 56 $\frac{1}{2}$ parts of oleic acid (commercially pure) are heated with stirring at a temperature of 240° to 250°C ., (substantially dry, inert gas being vigorously bubbled through the mixture simultaneously), for approximately four hours, until the free fatty acid content of the mixture is approximately $\frac{1}{2}$ of 1% or less. The product is now cooled in an inert atmosphere.

100 parts of this product, which consists essentially of a mixture of diglycerides, dissolved in 300 parts of isopropyl ether, are refluxed for two hours with 25 parts of finely divided phosphorus pentoxide, care being taken to exclude moisture from contaminating the reaction mixture.

The mixture is cooled, insoluble material is filtered off, the ether is evaporated off and the product, which consists essentially of esters of phosphoric acid, may be used as such or it may be neutralized with alkaline agents such as sodium hydroxide, sodium carbonate, or the like.

Example I.—80 parts of finely divided phosphorus pentoxide are stirred into a solution of 100 parts of monostearine dissolved in 1000 parts of isopropyl ether (free of moisture and alcohol). This mixture is continually stirred and heated sufficiently under reflux condenser to maintain it substantially at the boiling point of the mixture, for two hours. The batch is now cooled to room temperature. The ether, which contains the principal portion of the reaction product in solution, is decanted from the undissolved material. The ether is distilled off and the residue is aerated to drive off the remaining small pro-

portion of ether. The product consists essentially of esters of phosphoric acid in the form of a white, pulverizable solid with high potency with respect to the interface properties discussed hereinabove.

Many other more or less lipophile materials which have at least one unesterified hydroxy group capable of reacting with phosphorus pentoxide, may be converted into my interface modifiers by the methods described herein, particularly as in Example I, in general, by causing approximately equal weights of phosphorus pentoxide to react with the organic substance in the presence of a solvent such as isopropyl ether.

Other solvents may be used and the proportion of phosphorus pentoxide is subject to considerable variation, subject to the limitations discussed at great length hereinabove. In all cases interfacially active esters of phosphoric acid possessing a lipophile group and a hydrophilic phosphate group are obtained.

The physical properties of the product, such as color and consistency, depend a great deal upon the starting material. Melissyl alcohol, for example, gives a rather hard, dark phosphate ester, whereas cetyl alcohol produces a nasty material of a dark color. The solubility or dispersibility in oils and fats also varies with the relationship of the lipophile group to the hydrophilic phosphate group. The more potent materials produce noticeable interfacial effects in proportion as small as $\frac{1}{4}$ to $\frac{1}{2}\%$. Examples of the more or less lipophile materials possessing at least one hydroxy group reactive to phosphorus pentoxide, which are suitable for the purposes of my invention, in addition to those already mentioned herein, are as follows:

Hexyl alcohol, octyl alcohol, dodecyl alcohol, myristyl alcohol, oleyl alcohol, octadecyl alcohol, ceryl alcohol, melissyl alcohol, castor oil, mono fatty acid esters of ethylene glycol, mono fatty acid esters of diethylene glycol, mono fatty acid esters of glycerine, fatty acid esters of polyglycerols with at least one hydroxy group reactive to phosphorus pentoxide, cetyl glycerol ether, lauryl ethylene glycol ether, myristyl diethylene glycol ether, other alkyl ethers with at least one hydroxy group reactive to phosphorus pentoxide, and other more or less lipophile substances with at least one hydroxy group reactive to phosphorus pentoxide. All of these materials give reaction products with phosphorus pentoxide which comprise esters of phosphoric acid having a lipophile portion and a hydrophilic phosphate portion and with marked interfacial activity of the kind discussed at great length hereinabove, making them very valuable as addition agents in confections and the like.

My interface modifiers may be dried or further purified, decolorized or deodorized, or diluted by incorporation of oils or fats, or otherwise treated. The neutralization of the reaction products of my invention in general seems to impart definite improvements in potency, stability, color, consistency, etc. The unneutralized product, sometimes of a dark brown color, becomes lighter when treated with a neutralizing agent, a dark brown product usually attaining a straw color. Indeed, the color may be taken as an index in carrying out the neutralizing step. Usually the product becomes less fluid when neutralized, and is generally better suited to the purpose intended.

Example J.—Substantially water free glycerine is polymerized, preferably with the aid of an alkali catalyst, until it has an average molecu-

lar weight corresponding to a diglycerol. 166 parts of the polymerized product, 180 parts of oleic acid, and 105 parts of stearic acid of good commercial grade are mixed together and heated to a temperature of about 220° to 225° C. and maintained at that temperature for approximately two hours, the reaction mixture in the meantime being continuously stirred. Atmospheric oxygen is kept out of contact with the mixture, preferably by maintaining an atmosphere of an inert gas at the surface, for example by bubbling carbon dioxide through the mixture continuously. The reaction should be allowed to continue until the acidity of the mixture is below 1%, the time, temperature and conditions described usually being suitable to produce this result. The product is then allowed to stand and any unreacted polyglycerol present is allowed to settle out.

To 450 parts of the mixed polyglycerol esters prepared as in the preceding paragraph, while at a temperature of approximately 60° C., 75 to 100 parts of fine phosphorus pentoxide are slowly added. A jacketed vessel may be employed to control temperature. The product is heated to approximately 120° C. and kept at that temperature for about twenty minutes. It is then removed from the vessel and centrifuged to remove insoluble materials, consisting for the most part of phosphorus pentoxide and adhering or loosely combined organic matter.

400 parts of the pretreated product are returned to the jacketed vessel and at 50° C. fifty parts of fine phosphorus pentoxide are added slowly thereto. The reaction mixture is heated to about 70° C. and the temperature then rises to about 95° C. The product is kept at this temperature for a few minutes, the total time for the entire esterification step being about twenty-five minutes.

The esterified product is neutralized suitably either by the use of sodium carbonate, as described in Example D, or by the use of ammonia, or by employing any other suitable alkaline organic or inorganic neutralizing agent. In general, very good results are obtained if the hydrogen ions of the hydrophilic phosphate group are replaced by either sodium or ammonium ions.

It should be understood that the pretreatment conditions described generally in the foregoing part of the specification and more specifically in the various examples hereinabove may be varied as to temperature, time, proportion and kind of pretreating agent, and for each set of pretreating conditions, a corresponding potency is obtained.

In each of the examples given in which the pretreatment step is employed, the pretreating agent, apparently in a somewhat altered form, is removed by centrifuging. Other adaptable and suitable methods of removal conventionally employed in the chemical industries for separation processes may be used. Moreover, the pretreating agent, such as phosphorus pentoxide, may be allowed to remain. I have found, however, that even when phosphorus pentoxide is used for the pretreating step and also for the final esterification step, more phosphorus pentoxide is required in the esterification step if the phosphorus pentoxide used in the pretreatment step be not removed. Furthermore, a higher temperature must be employed in the final esterification step. While the resulting product may have more potency than a product produced without the use of the pretreatment step, such product, however, is not as potent by any means as the prod-

uct produced when the pretreating agent is removed after the pretreating step.

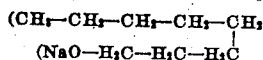
Throughout this specification, I have employed the term "lipophile" to designate organic radicals with fatty characteristics. In general, such radicals consist primarily of carbon and hydrogen, although they may include ether and/or ester linkages. I have employed this term "lipophile" to denote that the radical so designated has a distinct affinity for oils, fats, waxes and other fatty materials, and imparts a tendency to the molecule, of which it is a part, to be wetted by fatty materials.

I have employed the term "hydrophile" throughout this specification primarily to denote properties antithetical to the "lipophile". In counter-distinction to the "lipophile" radicals, the "hydrophile" radicals consist primarily of hydrogen and oxygen and the "hydrophile" characteristics are imparted primarily by hydroxy groups attached to carbon or phosphorus. The hydrophilic character manifests itself by an affinity for water and aqueous media, and the hydrophile radical imparts to the molecule, of which it is a member, a tendency to be wetted by water and aqueous media. The degree or extent of the hydrophilic character is dependent upon the number of hydroxy groups and their location in the molecule, and is also influenced by the number and character of lipophile groups with which they are associated in the molecule.

The polyhydroxy substances which are the linking substances between the lipophile group or groups and the hydrophile phosphate group may be conveniently considered as falling into two groups. The first of these groups includes compounds containing less than four esterifiable hydroxy groups and is exemplified by glycerine, glycol and polyglycols. The second group contains those substances which have more than three esterifiable hydroxy groups, examples of which are the sugars and sugar alcohols, the polyglycerols such as di- and tri-glycerol, etc. It will be understood that my compounds may have one or more lipophile radicals and one or more hydrophile phosphate radicals attached to the polyhydroxy substance. Thus, for example, I may have the mono-phosphate of the di-oleic acid ester of sucrose, or the di-phosphate of the di-oleic acid ester of sucrose. Similarly, I may have the di-stearic or other fatty acid ester of di- or tri-glycerol mono- or di-phosphate. In a similar way, as described above, instead of the acyl derivatives of the polyhydroxy substances I produce the corresponding alkyl derivatives.

As I have described above, my compounds may contain either ester or ether linkages. Any known methods of etherifying polyhydroxy substances may be employed. The following examples are illustrative:

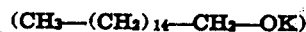
Example K.—Sodium octylate



is treated with a 25% molal excess of glycerine alpha bromhydrin. The mixture is heated under reflux with exclusion of moisture and with stirring until the anticipated amount of sodium bromide has formed. The sodium bromide is filtered out of the hot reaction mixture and the product, namely, glycerol alpha octyl ether, is separated from the excess mono bromhydrin by fractional distillation under reduced pressure. The ether is pretreated with phosphorus pent-

oxide and subsequently reacted with a further quantity of phosphorus pentoxide to form the phosphate ester, by the general procedure described in Examples C or D hereinabove.

Example L.—Potassium cetylate



is reacted with excess ethylene glycol chlorhydrin by the procedure described in Example K, to form the glycol mono octyl ether. This is then pretreated with P_2O_5 and then finally esterified with a second portion of P_2O_5 to form a phosphoric acid ester of cetyl glycol ether. This may be neutralized with ammonia or some other alkaline or potentially alkaline material to give salts of the cetyl glycol ether phosphate.

Many of the products above described may be added in suitable proportions to a treating bath containing an aqueous medium, with or without an additional substance, such as for example, alkalis, mordants, dyes, color discharging reagents, H_2O_2 , color reducing agents, oils, sulfonated oils, mordanting salts, fabrics and other reagents or substances used in treating baths, and the treating bath so formed can be employed with satisfaction in many of the arts in which interface modification is desired. For example, dyeing, bleaching, scouring, and otherwise treating fabrics, fibers and other materials in a treating bath of this character are productive of good results. Also in the stuffing of leather, dyeing, and otherwise treating furs, and in many other arts, a treating bath employing the materials of my invention may be used. In flotation of ores it may be used in connection with other reagents to modify the interface between the finely divided ore and the aqueous medium. The substances of my invention, particularly when made in accordance with the pretreatment step, possess unusually excellent emulsifying properties for the making of water-in-oil emulsions.

Many of the products described hereinabove are very valuable as interface modifiers in confections such as chocolate mixes intended as coverings for cakes, candies and the like, or other products of the general type described in my prior application, Serial No. 710,893. In general, these treating substances are improved if the pretreatment step is employed for "conditioning" the ester or ether of the polyhydroxy substance before one or more free hydroxy groups thereof are esterified with phosphoric acids or the like. It is understood, therefore, that I do not limit the use of the pretreatment step to the particular examples given but such pretreatment step may be used as well in the preparation of other compounds of my invention independently of the type of material used as a source of phosphoric acids, provided, of course, that the material possesses the inherent property of forming phosphoric acid esters, or the particular embodiment of the method for carrying out the esterification. The pretreatment step as previously described may be modified in several respects while still obtaining the advantage of improvement in potency of the final esterified product.

In employing my interface modifiers in products such as confections, it will be understood that the character of the improvement effected by the introduction of such interface modifiers naturally varies with the composition at hand and to some extent also with the particular phosphoric acid ester employed. In general all of the esters produced by the use of the pretreatment step show an improvement in viscosity re-

duction in confections over the same substances produced without the pretreatment step.

The improvement in chocolate and confectionery batches and similar substances is not entirely a matter of viscosity reduction. For example, in a conventional chocolate mix such as one containing 148 parts of powdered sugar (6-X cane sugar), 52 parts of cocoa powder (12% fat content), 100 parts of cocoa butter and flavoring, the principal improvement is a substantial reduction in viscosity. In a confection such as toffee consisting, for example, of 60 parts of cocoanut stearine, 140 parts of 4-X cane sugar, 20 parts of invert sugar, and 20 parts of water, wherein the mix is boiled at about 285° F., and the fat must emulsify and remain emulsified at this relatively high temperature, the improvement is largely one in the ease of the emulsification and the stability of the emulsion obtained. In still other preparations, additional improvements are found such as the character of texture, appearance and/or flavor; but it is to be noted that, in every instance, whatever the character of the improvement at hand, the physical-chemical mechanism is one of interface modification effected by the character of the interface modifiers which I describe herein.

The amount of interface modifying agent employed in, for example, the confection, though subject to considerable latitude, will ordinarily vary between approximately one-fourth percent and three percent, depending upon the nature of the product, the function desired, and the character of the phosphoric acid ester used. In general, the phosphoric acid esters, by the use of the pretreatment step, may be used in relatively smaller amounts, or they may be used in the same amounts and somewhat greater improvement obtained.

As one example of the advantages obtained from the use of my invention, a conventional chocolate mix may be considered. One hundred parts of a given chocolate mix composition were found to require about 85 seconds at 43° C. to pass through a given orifice. In making a test of this character, the mix is milled warm according to the usual custom for about 15 minutes and then allowed to cool to about 43° C., at which temperature the test is made. About one-quarter percent of one of the materials of my invention, prepared, for instance, as in Example D, when added to such a mix and thoroughly dispersed therethrough, will reduce the time of flow to 36 seconds, all conditions remaining the same. The same addition agent produced without the pretreatment step reduces the viscosity somewhat less so that the time of flow is 45 seconds, all other conditions remaining the same.

The reduction of viscosity, of course, may be taken advantage of in various ways and may also be employed for the purpose of economizing in the proportion of fat used. That is to say, a given viscosity may be obtained, other things being equal, with a substantially smaller proportion of the fat ingredient, when a phosphoric acid ester of the kind described herein is incorporated in the mixture.

The most desirable manner of incorporating the interface modifiers of my invention, in the case of, for example, confections, is to dissolve them in the fat content of the confection in which they are used. The usual fats employed are cocoa butter, so-called pressed butter, cocoanut stearine, dairy butter, hydrogenated oils and other oils, fats and fatty materials.

As applied to use in confections, the invention has been considered from the standpoint of reduction in viscosity, but, as indicated above, many other improvements manifest themselves in various forms to those skilled in the art to which the invention relates. For example, the improvements effected make possible lower enrobing temperatures; they make possible longer cooling periods, thereby permitting longer time out of tunnels; a greater range of working temperatures on the enrobing machine is possible; tempering is more uniform and gradual; in the cooking of toffees, by virtue of the fact that a far superior and a much more stable emulsion is obtained, the cooking is more flexible and tolerates considerably more abuse and variation than heretofore, without detrimental effects on the ultimate product; the tendency to "blooming" is considerably diminished and delayed. In many instances additional desired characteristics inure to the products concerned, by virtue of the diminished fat content.

A valuable feature of many of the products of my present invention is that they can be produced in the form of a substantially impalpable powder, and are, therefore, conveniently and readily incorporated into products of the character described. For example, many of the products of my invention may be sprayed into a cold atmosphere whereby the finely divided material of the spray is congealed and takes substantially a powder-like form. Still other ways of producing the substances in a convenient and desirable condition for use can be used.

The invention, as it applies to confections and confection-like materials, is of value under any circumstances in which a comminuted material such as sugar, cocoa powder, powdered milk, powdered egg whites, or other powdered or finely divided material is dispersed in a fatty material.

While I have described several methods for the preparation of the materials of my invention, it must be understood that the scope of the invented class of substances is by no means limited by these methods. Other convenient methods may be used. This also applies, and particularly so, to supplementary procedures of purification or isolation which lie strictly within the province of skill of any qualified chemist whose procedures in each instance must be governed by the properties of the materials concerned and by the degree or the character of the purity desired.

Similarly, in the neutralization of the phosphate group or groups, considerable latitude and modification may be employed. While the phosphate group may be left unneutralized, I find that, in general, the products are more suited to the purpose for which they are intended if they are treated with a suitable inorganic or organic anti-acid agent. Examples of inorganic and organic anti-acid agents which may be used satisfactorily are bicarbonates, potassium hydroxide, potassium carbonate, metallic sodium, sodium hydroxide, sodium carbonate, sodium oxide, ammonium hydroxide, ammonia gas, and other anti-acid materials of the alkali earth group, sodium stearate, calcium stearate, ethanalamines, such as the mono-, di-, and triethanolamine, or mixtures thereof, and also other anti-acid materials in which case the hydrogen of the phosphate group or groups is replaced by a cation such as sodium, potassium, ammonium, calcium, magnesium, aluminum, zinc, etc. It will be understood that by the term "cation", as used throughout the specification and claims, is meant such

elements as are mentioned herein and, in general, atoms or radicals which are regarded as bearing a positive charge.

Whenever the term "polyhydroxy substance" is used in the specification and claims, it will be understood to cover substances having at least two esterifiable or etherifiable hydroxy groups independently of any carboxylic groups which may be present in the same molecule.

The term "residue", as used throughout the specification and claims, is employed in its ordinarily understood chemical significance. For example, where one of the hydroxyl groups of glycerine is esterified with a fatty acid or etherified with an alcohol, and another of the hydroxyl groups of the glycerine is esterified with a phosphoric acid, that which remains of the glycerine molecule, for example,



is the "residue" of the polyhydroxy substance, in this case glycerine.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. The process of preparing esters of phosphoric acids which comprises subjecting a lipophile material having at least six carbon atoms and at least one free hydroxy group to preliminary treatment with a proportion of phosphorus pentoxide at a temperature not substantially less than 115 degrees C. whereby said lipophile material is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said lipophile material, physically removing said phosphorus and adhering material, and then reacting the "conditioned" material with a proportion of phosphorus pentoxide at elevated temperatures to produce the esters of phosphoric acids.

2. The process of claim 1, wherein the resulting esters are neutralized at least in part.

3. The process of claim 1, wherein the lipophile material is a partial higher fatty acid ester of a polyhydroxy substance of the group consisting of glycerol, glycol, polyglycerols, polyglycols, sugars, sugar alcohols, and polyhydroxycarboxylic acids.

4. A process of preparing esters of phosphoric acids which comprises subjecting a lipophile material having at least six carbon atoms and at least one free hydroxy group, at a temperature of at least 115 degrees C. but below the temperature of decomposition of the reactants or the finished product, to preliminary treatment with a proportion of a derivative of phosphorus capable of forming an ester of a phosphoric acid, whereby said lipophile material is "conditioned" without effecting any appreciable organic combination of the derivative of phosphorus with said lipophile material, physically removing said derivative of phosphorus and adhering material, and then reacting the "conditioned" lipophile material, at a temperature between 80 degrees and 140 degrees C., with a derivative of phosphorus capable of forming an ester of a phosphoric acid to produce the esters of the phosphoric acids.

5. The process of claim 4, wherein the derivative of phosphorus is, in each instance, phosphorus pentoxide.

6. The process of claim 4, wherein the lipophile material is a partial higher fatty acid ester of a polyhydroxy substance of the class con-

sisting of glycerol, glycol, polyglycerols, polyglycols, sugars, sugar alcohols, and polyhydroxycarboxylic acids.

7. The process of preparing esters of phosphoric acids which comprises subjecting a higher fatty acid ester of glycerin having at least one free glycerin hydroxy group, the higher fatty acid radical of said ester containing at least six carbon atoms, to preliminary treatment with a proportion of phosphorus pentoxide, at a temperature of about 115 degrees C. to about 120 degrees C., whereby said ester is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said ester, physically removing said phosphorus pentoxide and adhering material, and reacting the "conditioned" product at elevated temperatures with a derivative of phosphorus capable of forming an ester of a phosphoric acid to produce the esters of the phosphoric acids.

8. The process of claim 7, wherein the derivative of phosphorus is phosphorus pentoxide.

9. The process of preparing esters of phosphoric acids which comprises subjecting unsaturated higher fatty acid esters of glycerin containing at least one free glycerin hydroxy group, the higher fatty acid radical of said ester containing from twelve to eighteen carbon atoms, to preliminary treatment with a proportion of phosphorus pentoxide, at elevated temperatures, whereby said esters are "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said esters, physically removing said phosphorus pentoxide and adhering material, and then reacting the "conditioned" product at elevated temperatures with a proportion of phosphorus pentoxide to produce said esters of phosphoric acids.

10. The process of preparing esters of phosphoric acids from a mixture of mono- and diglycerides resulting from the re-esterification of cottonseed oil with glycerin, which comprises subjecting said mixture of mono- and diglycerides, at a temperature of about 115 degrees C. to about 120 degrees C., to preliminary treatment with a proportion of phosphorus pentoxide whereby said mixture of mono- and diglycerides is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said mono- and diglycerides, physically removing said phosphorus pentoxide and adhering material, and thereafter introducing a proportion of phosphorus pentoxide into the "conditioned" product and reacting the resulting mixture at a temperature of about 80 degrees C. to about 100 degrees C. to produce the esters of the phosphoric acids.

11. The process of preparing esters of phosphoric acids which comprises subjecting normally liquid vegetable oil fatty acid esters of glycerin containing at least one free glycerin hydroxy group to treatment with a proportion of phosphorus pentoxide at elevated temperatures whereby said esters are "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said esters, physically removing said phosphorus pentoxide and adhering material, then introducing into the "conditioned" product a proportion of a derivative of phosphorus capable of forming an ester of a phosphoric acid, and reacting the resulting mixture to produce the esters of the phosphoric acids.

12. The process of preparing esters of phosphoric acids which comprises contacting an ester

of the class consisting of higher fatty acid monoglycerides, higher fatty acid diglycerides, and mixtures thereof, the higher fatty acid radical of which contains at least six carbon atoms, with about 10% of phosphorus pentoxide, at a temperature of about 115 degrees C. to about 120 degrees C. for at least 20 minutes, whereby said ester is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said ester, physically removing said phosphorus pentoxide and adhering material, and then introducing a proportion of phosphorus pentoxide into the "conditioned" material and reacting the mixture for at least 10 minutes at a temperature of at least 80 degrees C. to produce the esters of the phosphoric acids.

13. The process of preparing esters of phosphoric acids which comprises contacting a higher fatty acid ester of glycerin having at least one free glycerin hydroxy group, the higher fatty acid radical of said ester containing from twelve to eighteen carbon atoms, with a proportion of phosphorus pentoxide, at a temperature of at least 115 degrees C., whereby said ester is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said ester, physically removing said phosphorus pentoxide and adhering material, and reacting the "conditioned" product with a proportion of phosphorus pentoxide at an elevated temperature to produce the esters of the phosphoric acids, and then treating the resulting product with a neutralizing agent to decrease the acidity of the resulting reaction product.

14. The process of preparing esters of phosphoric acids which comprises contacting a product consisting primarily of monoglyceride, and prepared by re-esterification of cottonseed oil hydrogenated to an iodine value of approximately 65 with a large excess of glycerol, at a temperature between approximately 115 degrees C. and 140 degrees C. for at least twenty minutes, with an amount of phosphorus pentoxide whereby said monoglyceride is "conditioned" without effecting any appreciable organic combination of said phosphorus pentoxide with said monoglyceride, physically removing said phosphorus pentoxide and adhering material, and then reacting the "conditioned" monoglyceride product with a proportion of phosphorus pentoxide, said reaction being carried out at a temperature of at least 80 degrees C. to produce the esters of the phosphoric acids.

15. The process of preparing esters of phosphoric acids which comprises subjecting a higher fatty acid ester of an aliphatic polyhydroxy substance, the higher fatty acid radical of said ester containing at least six carbon atoms, said ester containing at least one free hydroxy group attached to the polyhydroxy nucleus, to treatment, at a temperature between approximately 115 degrees C. and 140 degrees C., with a derivative of phosphorus capable of forming an ester of a phosphoric acid whereby said ester is "conditioned" without effecting any appreciable organic combination of the derivative of phosphorus with said ester, physically removing said derivative of phosphorus and adhering material, and then reacting the "conditioned" ester with a derivative of phosphorus capable of forming an ester of a phosphoric acid to produce the esters of the phosphoric acids.

16. The process of preparing esters of phosphoric acids which comprises subjecting a lipophile material, selected from the group consist-

ing of higher molecular weight aliphatic ethers and esters of aliphatic polyhydroxy substances, the higher molecular weight radical of which contains at least six carbon atoms, said lipophile material having at least one free hydroxy group, at elevated temperatures, to treatment with phosphorus pentoxide, whereby said lipophile material is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said lipophile material, physically removing said phosphorus pentoxide and adhering material from the lipophile material, and then reacting the remaining lipophile material with a derivative of phosphorus capable of forming an ester of a phosphoric acid to produce the esters of the phosphoric acids.

17. Reaction products formed by subjecting a lipophile material having at least six carbon atoms and at least one free hydroxyl group to treatment with a proportion of phosphorus pentoxide at a temperature of at least 115 degrees C. whereby said lipophile material is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said lipophile material, physically removing said phosphorus pentoxide and adhering material, and then reacting the "conditioned" lipophile material, at elevated temperatures, with a proportion of a derivative of phosphorus capable of forming an ester of phosphoric acid to produce an ester of a phosphoric acid.

18. Reaction products formed by subjecting lipophile material, selected from the group consisting of higher molecular weight aliphatic ethers and esters of polyhydroxy substances, the higher molecular weight radical of which contains at least six carbon atoms, said lipophile material having at least one free hydroxyl group directly attached to the polyhydroxy nucleus, to treatment with a proportion of phosphorus pentoxide at a temperature of about 115 degrees C. to about 120 degrees C., whereby said lipophile material is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said lipophile material, physically removing said phosphorus pentoxide and adhering material, and then reacting the remaining lipophile material with a proportion of phosphorus pentoxide at elevated temperatures to produce an ester of a phosphoric acid.

19. The product of claim 18, wherein the final product is neutralized at least in part.

20. Reaction products formed by contacting a higher fatty acid ester of glycerin having at least one free glycerin hydroxy group, the higher fatty acid radical of said ester containing at least six carbon atoms, with a proportion of phosphorus pentoxide at a temperature of at least 115 degrees C. but below the temperature of decomposition of the reacting ingredients or the finished product, whereby said ester is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said ester, physically removing said phosphorus pentoxide and adhering material, and reacting the "conditioned" product with a proportion of phosphorus pentoxide at a temperature of at least 80 degrees C. to produce an ester of a phosphoric acid.

21. Reaction products formed by contacting an ester of the class consisting of higher fatty acid monoglycerides, higher fatty acid diglycerides, and mixtures thereof, the higher fatty acid radical of said monoglycerides and diglycerides having from twelve to eighteen carbon atoms, with a proportion of phosphorus pentoxide, at a tem-

perature of at least 115 degrees C., whereby said ester is "conditioned" without effecting any appreciable organic combination of the phosphorus pentoxide with said ester, physically removing
5 said phosphorus pentoxide and adhering material, and then introducing a proportion of phosphorus pentoxide into the "conditioned" product and reacting the mixture at a temperature of from about 80 degrees C. to about 140 degrees C. to
10 produce an ester of a phosphoric acid.

22. Reaction products formed by contacting a product, consisting primarily of monoglycerides and prepared by re-esterification of cottonseed oil hydrogenated to an iodine value of approximately

65 with a large excess of glycerol, with phosphorus pentoxide, at a temperature between approximately 115 degrees C. and 140 degrees C. for at least twenty minutes, whereby said monoglycerides are "conditioned" without effecting any
5 appreciable organic combination of the phosphorus pentoxide with said monoglycerides, physically removing said phosphorus pentoxide and adhering material, and then reacting the "conditioned" monoglyceride product with phosphorus
10 pentoxide at a temperature of from about 80 degrees C. to about 120 degrees C. to produce an ester of a phosphoric acid.

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