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WETTING AGENT AND DETERGENT AID

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12 Claims. (Cl. 260—461)

This invention relates to improved detergent aids and wetting agents. More particularly, it relates to high wetting power salts of phosphoric acid partially esterified by hydroxy aromatic compounds containing suitable hydrocarbon substituent groups.

By wetting agent is meant substances which improve spreading of surface coatings, increase spreading and penetrating power of liquids, such as aqueous solutions and oils, and which may act as detergent aids, emulsifying agents, and dispersing agents, all of these actions depending somewhat upon changes of interfacial and surface tension.

The wetting power of these agents can be evaluated by simple and rapid methods which measure the relative time taken for an aqueous solution of an agent to thoroughly penetrate, under prescribed conditions, a fabric or skein of fibres having a prescribed composition, form, and size. Although these methods more particularly compare the penetrating and detergent aiding action of the agents, they indicate, in general, the capacities of the agents to perform other wetting functions.

Although wetting agents and detergent aids have been prepared by neutralizing acid esters formed by reacting gaseous olefins with phenol in the presence of sulfuric acid, it has been found that salts of phosphoric acid partially esterified by phenolic compounds are properly constituted for high wetting power when the phenolic compounds contain suitable hydrocarbon constituents prior to esterification with phosphoric acid or its condensible derivatives. While the salts of sulfuric acid partially esterified by alkylated phenols can be prepared by having the alkylation step occur during the esterification, there are applications in which such salts are less desirable due to corrosiveness tendencies of their hydrolysis products.

An object of this invention is to produce from phenolic compounds and phosphoric acid or its condensible derivatives, wetting agents and detergent aids which have high wetting and detergent effectiveness with restricted hydrolysis.

Another object of this invention is to prepare acid esters of phosphoric acid which on neutralization produce stable salts having wetting powers comparable to the most effective ester salt derivatives of sulfuric acid, and in some applications, even greater wetting powers, yet without corrosive tendencies of the sulfuric acid ester salts.

A further object of this invention is to provide mono- and di-esters of alkyl phenols and phosphoric acid and to provide such esters which can be reacted with alkali metal bases, to form naphtha-insoluble and ether-insoluble salts having high wetting numbers in aqueous solutions. Other specific objects will appear from the description which follows.

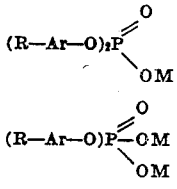
These objects are achieved by partially esterifying phosphoric acid, or a halogen derivative thereof, with selected phenolic compounds to obtain acid esters which are subsequently neutralized to form the desired salts. Suitable alkyl phenols to be used as starting materials may be obtained by alkylation of lower phenols present in coal tar fractions or tar acids. Petroleum phenols, per se, are very suitable. But, the phenolic compounds are preferably selected when they have alkyl side chains, either simple straight chain or cyclic, containing sufficient saturated carbon atoms to make a total of about 5 to 20 carbon atoms per molecule of acid ester formed in the esterification. As a rule, the wetting power decreases, while the detergent power increases, with increase in the size of the hydrocarbon substituent. For optimum results, the phenolic compounds having hydrocarbon side groups containing about 3 to 10 saturated carbon atoms per molecule, are preferred for producing di-ester salts. More exactly, the di-ester salt should contain 5 to 20 alkyl or cycloalkyl carbon atoms per molecule, that is, it is formed from the reaction of alkyl phenols having an average of 2.5 to 10 alkyl carbon atoms per molecule. In forming the mono-ester, it is best to esterify a phenol having at least 5 carbon atoms in the hydrocarbon side chain.

Synthetic alkyl phenols may be prepared by any of the known methods of alkylation. Suitable methods for their preparation are disclosed in U. S. Patent 1,948,287 of February 20, 1934, to Hyym E. Buc and Ruben Schuler, and U. S. Patent 1,954,985 of April 17, 1934, to Hyym E. Buc. These patents describe methods for alkylating phenolic compounds such as phenol, cresols, etc., with olefinic hydrocarbons having more than 2 carbon atoms per molecule and similar reactants. They indicate reactions of alkylating compounds with the phenolic compounds in the presence of strong sulfuric acid at controlled temperatures. The alkyl substituents formed may be normal, iso, secondary, or tertiary.

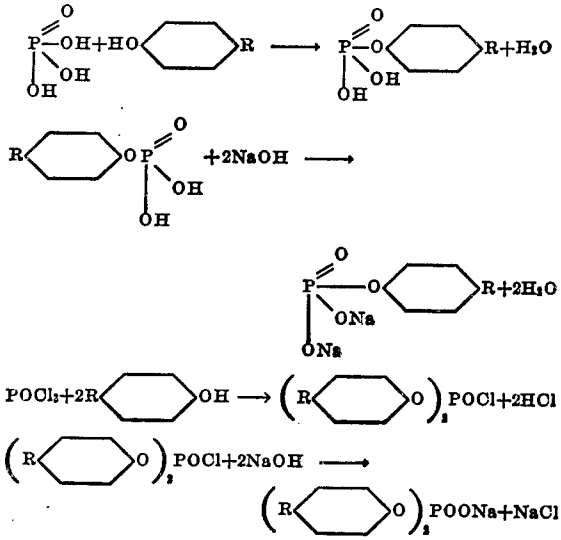
The phenolic compounds may contain more than one alkyl substituent and other aliphatic or cycloaliphatic hydrocarbon substituents which

supply the proper number of saturated carbon atoms which may be designated as paraffinic carbon atoms. Petroleum phenols which to some extent simulate phenolic compounds containing a polymethylene or cycloalkyl side group, according to their hydrogen and carbon analyses, have been found to be as satisfactory as alkyl phenols of corresponding or even higher molecular weights. Polyalkyl phenols may be obtained by alkylating lower phenols with suitable alkylating agents such as alcohols, olefins, alkyl sulfates, and alkyl halides, and these alkylating agents may be obtained from cracked petroleum hydrocarbon products.

Compounds which are to be preferably produced according to the present invention may be represented as including types having the following generalized compositions and structures:



where R represents 1 or several alkyl substituents containing an average total of 5 to 20 saturated carbon atoms, Ar represents an aromatic nucleus, and M stands for a basic metal atom. It is to be noted that the salts may be formed from a mono- or di-ester of phosphoric acid, orthophosphoric acid being the esterifying acid in obtaining either the di- or mono-basic salt, meta- and pyrophosphoric acids being adapted for forming the di-basic salt, and halogen derivatives of the acid, e. g., $POCl_3$ or PCl_5 being used in some reactions to advantage in place of orthophosphoric acid. The desired partial esters containing the tervalent radical, $\equiv P{=}O$, are thus obtained by using pentavalent phosphorus compounds which on hydrolysis yield phosphoric acid. The following equations, wherein R represents a hydrocarbon side group, are typical of the reactions carried out:



The preferred methods of this invention for preparing high quality detergent aids will be understood from the following specific examples:

Example 1

To prepare a sodium salt of di(tertiary amylphenyl) phosphate, a one liter three-way flask fitted with a mechanical stirrer having a mercury seal, a reflux condenser, and a thermometer was charged with the following materials:

Tertiary amyl phenol	gms	164
$O{=}PCl_3$	gms	85
Toluene	cc	250

The above materials were stirred and heated to 118° C. for 20 hours. Hydrogen chloride gas was liberated copiously in the early part of the reaction and at the end of this time the evolution of hydrogen chloride gas was slight. The toluene and excess $POCl_3$ was distilled off and the residue was added slowly to stirred cracked ice. The aqueous solution was extracted with ether and the ether extract was neutralized by pouring gradually into a sodium carbonate solution. The entire neutralized solution was then transferred into a separatory funnel, and upon standing, two layers separated, the top layer containing ether and salt; the lower layer, water and salt. The layers were separated and each was evaporated to dryness. 33 grams of a white powder were obtained from the evaporated water layer. The evaporated ether layer was leached twice with 54° A. P. I. naphtha, leaving 95 grams of white powder which was naphtha-insoluble. The characteristics of the thus separated products as wetting agents and detergent aids were determined by the method of Draves and Clarkson as published in the "Proc. Am. Assoc. Textile Chem. Colorists" 1931, 109. The naphtha-insoluble ether extract product had the following wetting out characteristics:

Weight conc. percent	Wetting numbers		
	Neutral	+Ca 300 p. p. m.	In 0.3% H_2SO_4
	Seconds		
0.2	4	Ppt'd	Less than 300
0.1	44		
0.07	147		

Accordingly, the naphtha-insoluble salt formed a clear neutral solution with water and showed a high wetting power. In hard water solution containing 300 parts per million of calcium, the salt tended to precipitate. In acidified solution, the salt caused some turbidity.

In some cases, it was found advantageous to carry out the condensation of the phosphorus oxy chloride with the alkylated phenol in the presence of pyridine or an equivalent base. In most cases, however, the use of the base was found unnecessary.

In a second experiment using the same type of procedure as explained in the foregoing experiment, phenolic compounds from a petroleum oil fraction were reacted with $POCl_3$ to form the di-ester chlorophosphate, and the resulting chlorophosphate was neutralized with potassium hydroxide to obtain an ether-extracted naphtha-insoluble salt having the following wetting properties in a neutral aqueous solution:

Concentration of salt by weight in aqueous solution, percent	0.2	0.1	0.07
Wetting numbers in soft water, sec.	4.5	30	187

From these data it can be observed that the lower petroleum phenolic compounds, which comprise phenols containing paraffinic hydrocarbon side groups having a lower hydrogen to carbon ratio than is present in simple alkyl

groups, form simple aryl ester salts of phosphoric acid which are as effective in wetting power as the salts formed from the lower phenols. In the foregoing experiment, the petroleum phenol cut used had an average empirical formula of about $C_{3.3}H_{7.5} \cdot C_6H_4OH$. This deficiency of hydrogen in the saturated hydrocarbon substituent group is attributed to the presence of cycloalkyl groups, which makes the hydroxyaromatic compound partly simulate a naphthenic compound. The high petroleum phenols having more than 10 carbon atoms per molecule show an even greater deficiency of hydrogen in this respect and also show the presence of non-phenolic oxygen. Though these higher petroleum phenols tend to darken readily in color, which may preclude their use in forming wetting agents for some purposes, they have marked resistance to alkalies and high organic solvent solubility which is a valuable property in many respects.

In a third experiment, a mol of phosphoric acid was esterified with one mol of tertiary amyl phenol to obtain a mono-ester, which, in turn, was neutralized with two mols of sodium hydroxide to produce the corresponding di-sodium salt of the mono-ester, which was extracted by isopropyl alcohol. The ether-insoluble portion of the isopropyl alcohol extract made a clear .2% concentration solution with distilled water and showed a wetting number of 37 seconds, and in a .2% concentration in hard water containing 300 parts per million of calcium ion gave a perfectly clear solution having a wetting number of 25 seconds. Other normally liquid aliphatic alcohols may be substituted for the isopropyl alcohol in the extraction.

Such experiments demonstrate that the naphtha-insoluble di-ester salts of the phosphoric acid esters were particularly effective wetting agents and detergent aids in neutral aqueous solutions, while the ether-insoluble salts of the mono-esters were more effective in hard water solutions. While certain classes of alkyl and cycloalkyl phenols have been emphasized as being of major importance for selection in forming the improved wetting agents by esterification with phosphoric acid or its halogen derivatives, various modifications to improve performance under some conditions may be made. For example, aliphatic alcohols, naphthenic alcohols, or aralkyl alcohols may be used auxiliary to the phenols in forming the phosphoric acid esters. Phosphate ester salts of naphthenic and aromatic alcohols may be used as supplementary wetting agents. Also, other wetting-out substances containing hydrocarbon groups attached to negative inorganic functions, such as hydroxyl, amino, sulfonate, sulfate, and halogen groups, may be used in combination with the phosphate ester salts.

The wetting agents prepared according to this invention may be used for a large variety of purposes, including among others, for scouring and detergent actions in conjunction with soaps or other detergents, and for dispersing pigments or other suspensoids in liquid vehicles, e. g., paints, water, inks, dye baths, metal plating baths, spraying compositions, ore flotation mixtures, and lead treating baths. They may be used to improve cosmetics, the wetting of glue, the mixing of cement, the finishing of pastes, the removal of grease from steel, the spreading and penetrating power of oils, the breaking of petroleum and water emulsions of the type found in oil fields, the emulsification in lacquer formation, the absorption qualities of paper in paper manufacturing, etc.

This invention is not to be limited by the specific examples given nor by any theory advanced on the mechanism of operation, but only by the appended claims in which it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

I claim:

1. A base metal salt of a phosphoric acid ester containing at least one alkylaryl group and a total of 5 to 20 saturated carbon atoms in the alkyl radicals of said alkyl-aryl groups.

2. A mono-basic alkali metal salt of a phosphoric acid ester in which the ester groups consist in alkyl phenyl radicals containing an average total of 5 to about 20 alkyl carbon atoms per molecule of the salt.

3. A naphtha insoluble di-basic alkali metal salt of phosphoric acid partially esterified by alkyl phenol molecules containing an average total of 5 to 10 alkyl carbon atoms per molecule.

4. A di-basic alkali metal salt of a phosphoric acid ester in which the ester group consists in an alkyl phenyl radical containing a total of 5 to about 20 alkyl carbon atoms per molecule of the salt.

5. An ether-insoluble alkali metal salt of phosphoric acid partially esterified with an alkyl phenol containing 5 to 10 alkyl carbon atoms per molecule.

6. The preparation of improved wetting agents by a process which comprises condensing with a pentavalent phosphorus compound which hydrolyzes to phosphoric acid a limited quantity of phenolic molecules containing hydrocarbon substituents which have an average total of 5 to 20 saturated carbon atoms per molecule of the phosphorus compound condensed, the quantity of phenolic molecules also being limited to produce phosphoric acid esters in the condensation, and neutralizing resulting acid esters with a metal base to produce their ester salts.

7. A process as described in claim 6, in which the improved wetting agents are extracted from said ester salts by ether and leached with naphtha.

8. A process as described in claim 6, in which the improved wetting agents are extracted from said ester salts by a normally liquid alcohol and leached with ether.

9. The preparation of improved wetting agents and detergent aids by a process which comprises condensing phosphoric acid with alkyl phenols having an average of 2.5 to 10 alkyl carbon atoms per molecule and reacted in a quantity to produce phosphoric acid di-esters, then neutralizing resulting acid esters with an alkali metal base to obtain their ester salts.

10. The preparation of improved wetting agents by a process which comprises condensing phosphorus oxychloride with a limited quantity of phenolic compounds containing paraffinic hydrocarbon substituents having an average of 2.5 to 10 carbon atoms per molecule to obtain phosphoric acid di-esters, and neutralizing said acid di-esters with an alkali metal base to obtain their ester salts.

11. The preparation of improved wetting agents by a process which comprises condensing phosphoric acid with an alkyl phenol containing 5 to about 20 alkyl carbon atoms per molecule and reacted in a quantity to produce a phosphoric acid mono-ester, and neutralizing

the resulting acid ester with an alkali metal base to produce an ester salt.

12. A compound of the general formula

$$(R—Ar—O)_xPO(OM)_y$$

in which R represents at least one alkyl substituent containing an average total of 5 to 20 carbon atoms, Ar represents an aromatic nucleus, M represents a basic metal atom and x and y are whole numbers from 1 to 2, the sum of which is 3.

LOUIS A. MIKESKA.

DISCLAIMER

2,219,050.—*Louis A. Mikeska*, Roselle, N. J. WETTING AGENT AND DETERGENT AID. Patent dated Oct. 22, 1940. Disclaimer filed Sept. 18, 1946, by the assignee, *Standard Oil Development Company*.

Hereby enters this disclaimer to claim 1.

[*Official Gazette October 22, 1946.*]

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