

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF DISINFECTANTS AND PEST EXTERMINATING AGENTS

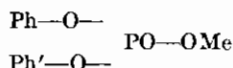
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This invention relates to the production of disinfectants and pest exterminating agents on the basis of aromatic hydroxyl compounds.

It is known that compositions of phenolic character, such as substituted phenols, naphthols, oxydiphenylmethanes and the substitution products of such compounds, possess excellent disinfecting power which, however, cannot be fully utilized for the reason that they are insoluble or very slightly soluble in water. It has been proposed to effect a solution of such compounds with the aid of dissolving partners like salts of the salicylic and cresotic acids and others, and particularly fatty acid and resin soaps. These soaps possess not only a great carrying capacity for many phenols but also great capillary activity and good wetting-out power and therefore also high penetrativity. Unfortunately, it was found out, however, that all such systems, especially if they show an alkaline reaction, tend to reduce the efficacy of the phenols, in consequence whereof the action of the agents on parasites is considerably weakened.

The invention proposes to use as dissolving aids or dispersion agents the salts of secondary phosphoric acid esters of the general formula



in which Ph and Ph' indicate a phenol, naphthol, oxydiphenylmethane or their substituted derivatives, above all their halogen-substituted derivatives, and Me stands for an alkaline metal or a nitrogenous base like ammonium, triethanolamine, etc. Aromatic hydroxyl compounds of this kind are briefly referred to below as "phenols."

Such bisphenolphosphates are capable not only of dispersing phenols or even of acting as dissolving partners to keep them in solution but are also active in lowering surface tension and in aqueous solution possess considerable wetting-out power. Above all, however, they have per se a remarkable bactericidal and fungicidal as well as a high disinfecting and pest destroying effect. Combined with phenols, they act as dissolving aids and dispersion agents and not only do not reduce the effectiveness of the phenols but positively increase it, frequently to such a point that the effects are potentiated and are overadditive.

A number of useful components are mentioned below without intending to restrict the invention to them.

Phenols within the meaning of the invention which are dispersed or colloidal dissolved but

which may serve also for building up bisphenolphosphates are for instance phenol, naphthol, oxydiphenylmethane and oxyquinoline and particularly the substitution products of these phenols, as cresols, xylenes, thymol, carvacrol, substituted naphthols and oxydiphenylmethane like benzylcresol and others. Particularly suitable appear to be combinations in which at least one constituent (dispersing medium or dispersed phenol) contains as a minimum a halophenol like chlorophenols, bromophenols, di- and trichlorophenols, chloronaphthols, chlorooxydiphenylmethanes like benzylchlorophenols and dichlorophenolmethanes and, above all, the extraordinarily effective substituted, i. e. alkylated, halophenols, such as chlorocresols, chlorothymol, chloroisothymol, benzylchlorocresol, etc.

When these phenols are to be used as dispersing media or dissolving aids in the form of bisphenolphosphates, they are converted by means of phosphoric acid or its derivatives, the chlorides or esters. Conversion can be effected in known manner, and the surprising fact discovered is that even the more complex alkyl halide phenols can be smoothly converted into the corresponding bisphenolphosphates. It is further possible to produce first monophenolphosphates in known manner and subsequently convert them into bisphenolphosphates so as to have an opportunity of incorporating therein different phenols, or to build up first the triphenolphosphates and to saponify them later on in suitable manner to form bisphenolphosphates, which may be effected by the action of saponifying acids and, above all, through saponifying bases. The following examples recite by way of explanation some of the methods of production without, however, restricting the invention to the disclosures made.

Example 1

From chlorothymol (excess) and phosphorus oxychloride, possibly with the addition of a diluent like nitrobenzene, xylene, etc., trichlorothymolphosphate is produced in known manner, possibly while adding a catalyst like aluminum chloride, iron chloride, zinc chloride, or the like. This compound may be produced also with the aid of sodium chlorothymol or by converting chlorothymol in alkaline aqueous or aqueous acetic solution with phosphorous oxychloride or even from phosphoric acid by conversion with chlorothymol or from an ester of phosphoric acid, possibly the triethylester, by conversion with chlorothymol.

¹/₂₀th mol trichlorothymolphosphate, melting

point 84°, is dissolved in alcohol and after addition of $\frac{1}{20}$ th mol. potassium hydroxide heated at boiling point for 10 hours. The alcohol is then evaporated, the residue taken up in water and the solution freed from split off chlorothymol. The bischlorothymolphosphate of potassium can be obtained from the solution by salting out with potassium carbonate. The free acid can be obtained by acidulating the salt solution by means of hydrochloric acid, extracting the bischlorothymolphosphoric acid with ether and recrystallizing the isolated acid from petroleum ether mixtures; it has a melting point of 134°.

To the sodium or potassium salt of this acid a phenol can be added to the easily ascertainable extent of the carrying capacity of a solution of these salts in water. Preferably, chlorothymol is used while equimolecular quantities are brought into solution and filtered off from smaller quantities of undissolved matter. The solution or dispersion may be produced also by retaining the amount of chlorothymol obtained during the preparation of the compound instead of separating it, this being probably the simplest manner of producing mixtures according to the invention.

Example 2

30 g. 5-chlorocarvacrol and 15 g. phosphorous oxychloride are slowly heated to 130° C. and kept at this temperature for 3 hours. The contents of the vessel are then subjected to fractional distillation, and the monochlorocarvacrolphosphoric-dichloride is then converted at a vacuum of 0.6 mm. at 123° to 125° C. and the bischlorocarvacrolphosphoric-monochloride at 190° to 192° C. The yield of dichloride amounts to approximately 5 g. and that of monochloride to about 24 g. The dichloride can be converted again into a bisphenol compound with the aid of chlorocarvacrol or another phenol, and the monochloride is decomposed with water to form a free acid. The sodium salt is soluble in ether.

To a solution of sodium or ammonium salt in ether is added approximately the semimolar amount of 4-chlorophenol or chlorothymol, whereupon the mixture is heated for some time and then evaporated to dryness. The residue is an excellent disinfectant.

Example 3

100 parts by weight bischlorothymolphosphate of potassium, 50 parts by weight commercial p-chloro-m-cresol and 100 parts by weight ethanol are dissolved in one another while being slightly heated. A 1:200 dilution in water kills suspensions of bact. coll. com. in about 10 minutes, a 1:1000 dilution kills instantly staphyloc. aureus and a 1:4000 dilution immediately destroys suspensions of streptococci. Even ground spores are instantly killed by a 1:400 dilution and after 5 to 10 minutes by a 1:1000 solution. The

solutions of the disinfectants in water prove to be typical colloidal solutions of excellent stability. Separation might happen with salts causing hardness of water, which may be prevented, however, by the addition of known substances like sodium tetrametaphosphate and similar isopolyphosphates, Turkey-red oil, sodium octadecenoyl-methylaminoethanesulfonate, sodium dodecanol-sulfate, etc.

Example 4

100 parts by weight potassium bischloroisothymolphosphate and 20 parts by weight commercial chlorothymol are together dissolved in ether and separated again as mixture by rapid evaporation of the ether. This mixture is dried in the vacuum. An aqueous solution of the mixture applied to vegetable germs show about the same effect as the preparation of Example 3. The effect upon spores was even considerably greater in spite of a smaller content of free phenol.

Example 5

100 parts by weight ammonium bis-p-chlorophenolphosphate or triethanolamine and 20 parts by weight 2,4-dichlorophenol are thoroughly triturated, whereupon enough ethanol is added to give a clear solution. The action of an aqueous solution obtained by dilution is only slightly less than that of Example 3.

If technical cresol mixtures serve for conversion into bisphenolphosphates which are used as carriers for such cresol mixtures or other phenol, the mixtures obtained will not be fully equal in effectiveness to those mentioned above but will be very cheap. Monophenolphosphates appearing during production need not be separated, as they do not cause any trouble but on the contrary add to the general effect. As stated before, the simplest procedure is to convert the phenols only partly into bisphenolphosphate and to use this, possibly together with monophenolphosphates that have appeared, as dispersion agent or dissolving aid for the non-phosphorylated portion of the phenols. The possibility of producing mixed bisphenolphosphates from different phenol components and using them has been mentioned already. For example, from oxydiphenylether-phosphatedichloride and chlorothymol in presence of pyridine a mixed bisphenolphosphate-monochloride was obtained from which the highly active salt can be produced.

Example 6

10 parts by weight potassium bischloroisothymolphosphate and 2 g. (1) chlorine (2) naphthol or 2 g. oxydiphenylmethane are dissolved in 12 parts by weight alcohol. The resulting solution has a strong bactericidal effect.

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