# Polyphosphates as Synergistic Antioxidants[1]

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THE antioxidant activity of phosphoric acid and some of its acid derivatives in combination with tocopherol in dry fats was first pointed out by Eckey (9). This acid has also been shown to be effective when used in fats containing nordihydroguaiaretic acid or gallic acid (12, 13).

The mechanism of the synergism was studied by Golumbic (11), who found that benzoquinone and tocoquinone, ineffective by themselves, had a powerful protective action on fats when combined with phosphoric acid. Considerable amounts of the corresponding quinols (hydroquinone and tocopherol) were recovered from the fat-quinone-phosphoric acid mixtures. It was postulated that phosphoric acid shifts the equilibrium quinol $\rightleftarrows$ quinone to the left and in addition catalyzes the cyclyzation of tocoquinone to tocopherol.

Calkins (4) further elucidated the probable mechanism by postulating as the first step the formation of a complex of the quinone and phosphoric acid, thus rendering the phosphoric acid fat soluble. The second step in the proposed mechanism is a reaction between the phosphorylated quinone and activated unsaturated fat, resulting in inactivated fat (thus breaking the chain reaction) and quinol.

Bailey and Feuge (1) also obtained great protective action when phosphoric acid was added to partially oxidized vegetable fats before deodorization. However there was no evidence of a reduction of the quinone in their work. In fact, less tocopherol remained after deodorization with phosphoric acid than after deodorization without phosphoric acid although the fat was stabilized by the phosphoric acid.

It was recently shown in this laboratory (17) that baking powder residues containing pyrophosphate as the acid ingredient had much greater protective action on fat than those containing various other acid ingredients, including orthophosphates. The conditions of these experiments were different from most of the work reported in the literature in that the fat was in close contact with an alkaline water phase, a situation representative of conditions in many baked products. The wide differences obtained between synergists in these baking powder experiments suggested the desirability of a re-evaluation of synergists under these conditions.

The present study is an investigation of the antioxidant activity of several synergists, including a group of polyphosphates not previously investigated, in two phase systems at controlled pH values in order to evaluate their probable effectiveness in complex foods containing water as well as fat.

## Materials and Methods

The phosphates used in this study together with information concerning their manufacture and properties were obtained through the courtesy of H. V. Moss, Monsanto Chemical Company, Anniston, Ala.

The method employed for obtaining contact between the water and fat has been fully described elsewhere (15, 17). In most of the experiments reported in this paper samples were considered rancid when the carotene appeared on visual inspection to be approximately half bleached. Peroxide numbers were not determined. It was felt that no additional accuracy was gained by the peroxide analysis since in some cases rancidity might develop only at one or two small spots on the paper, on account of imperfect contact with the synergist or to contamination during handling of the papers. High peroxide values were obtained on such samples at a time when oxidation had occurred only within a limited area of the total paper. By selecting the time of half bleaching, better agreement between duplicates was obtained.

The procedure for study of synergists in dry fats consisted of suspending the finely divided synergist directly in the melted fat plus carotene. The hot fat was then dropped from a pipette onto a Petri dish held on a cake of ice so that each drop of fat hardened immediately. If the fat were held at a uniform temperature and the dishes thoroughly cooled, a number of discs of fairly uniform diameter and thickness were thus obtained. These samples were stored at room temperature to prevent melting of the fat and settling out of the synergists. Rancidity was again followed visually by fading of the carotene. Since most of the synergists studied have limited solubility in fat, the degree of dispersion is dependent largely on fineness of grinding of the solid material.

TABLE I

Effect of Orthophosphates on Rancidity in Aqueous Fat Systems

| Solution in Contact with Fat | Days to Turn Rancid | |
|---|---|---|
| | Lard No. 1 | Lard No. 2 +.005% Tocopherol |
| Water control | 5 | 15 |
| $H_3PO_4$ (.01 molar) | 5 | 13 |
| $NaH_2PO_4$ (.01 molar) | 4 | 13 |
| $Na_2HPO_4$ (.01 molar) | 2 | 8 |
| $Na_3PO_4$ (.01 molar) | 2 | 8 |

## Results

*Preliminary Appraisal of Synergists.* Of a number of synergists tried, only citrate and the polyphosphates seemed sufficiently promising to warrant further investigation. Ascorbic acid and cysteine markedly accelerated rancidity when dissolved in water in contact with fats low in tocopherol (15). Threonine, leucine, phenyl alanine, methionine, and tryptophane, known to be effective synergists in dry fats (6), did not significantly protect lard (with or without added tocopherol) brought into contact with 0.1% aqueous solutions of the respective amino acids. Antioxidant indices ranged from 0.9 to 1.8. The poor showing of tartrate baking powders (17) eliminated tartrate from further study. Sorbitol had no protective effect either in the presence or absence of added copper or iron.

The effect of orthophosphates on rancidity in aqueous fat systems is shown in Table I. Neither phosphoric acid nor any of its sodium salts had any protective effect either on plain lard or on lard containing .005% tocopherol. While the acceleration

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obtained with the dibasic and tribasic sodium phosphates is partially due to the higher pH, orthophosphate buffers at pH 7.5 regularly accelerated rancidity slightly as compared to borate buffers or to sodium hydroxide solutions at the same pH.

*Antioxidant Effect of Citrate and Polyphosphates at pH 7.5.* Table II summarizes results of several experiments on this group of antioxidants. The control was .01 molar orthophosphate buffer, pH 7.5. In each case 0.2% solutions of the sodium salts of the synergists were prepared and their pH adjusted to 7.5 by addition of HCl or NaOH before dilution to the final concentration of 0.1%. No buffer was used in order not to complicate the results by addition of other ions. The synergists are arranged in order of their effectiveness. Degree of polymerization would appear to be of importance in determining antioxidant activity of the polyphosphates although molecular weights of the two most effective compounds, "hexametaphosphate" and Maddrell's salt, are not known (14).

The antioxidant effect of Maddrell's salt is of particular interest because of its very limited solubility. Suspensions containing .01% of this salt did not clear up even after some weeks of intermittent shaking. Nevertheless this suspension had marked antioxidant activity which increased with increasing concentration. The salt as manufactured contains a soluble fraction comprising about 2% of the total weight different in structure from the bulk of material. However the soluble impurities are not responsible for the antioxidant activity of this compound. The protective effect of the supernatant fluid obtained on centrifugation of such solutions was much less than that of the suspension and increased only slightly with a 100-fold increase in concentration. Evidently the finely suspended material is important, either as an antioxidant *per se* or for replenishment of the active fraction in solution as dissolved salt goes into the fat.

The "hexametaphosphate" used in these experiments, typical of the salts so designated commercially, is not a hexamer but a product polymerized to a much higher degree. It is of course completely water soluble. Its antioxidant activity is of the same order as that of Maddrell's salt. The "heptaphosphate" is also a mixture of polymers of various molecular weights.

The synergistic nature of the antioxidant effect of this group of compounds is clear from their activity with the same sample of lard with and without added tocopherol (Table II, Lard Sample No. 3). The keeping time of the lard containing tocopherol and synergist is always considerably greater than the additive effect of tocopherol and synergist separately. Such results do not of course rule out the possibility that the antioxidant effect is due to the counteracting of a catalyst, such as copper or iron.

TABLE II

Antioxidant Effect of Citrate and Polyphosphates at pH 7.5

| Synergist (.1%) | Days to Turn Rancid | | | |
|---|---|---|---|---|
| | Lard No. 1 | Lard No. 2 +.005% Tocopherol | Lard No. 3 | |
| | | | Plain | +.005% Tocopherol |
| Buffer control | 1.5 | 6 | 3 | 6 |
| Metaphosphate, trimer $(P_3O_9)^{3-}$ | .... | 14 | .... | .... |
| Pyrophosphate $(P_2O_7)^{4-}$ | 3 | 21 | .... | .... |
| Triphosphate $(P_3O_{10})^{6-}$ | 3 | .... | .... | .... |
| Citrate | 4 | 26 | 6 | 16 |
| "Heptaphosphate" $(P_7O_{22})^{9-}$ | 7 | .... | .... | .... |
| "Hexametaphosphate" $(PO_3)^{n-}$ | 15 | .... | 17 | 42 |
| Maddrell's salt $(NaPO_3)_x$ | 19 | 44 | 17 | 41 |

TABLE III

Antioxidant Effect of Various Synergists in Borate Versus Phosphate Buffers

| Synergist .1% | Days for Lard to Turn Rancid, pH 7.5 | |
|---|---|---|
| | Borate Buffer .01 Molar | Phosphate Buffer .01 Molar |
| Buffer control | 3 | 2 |
| Citrate | 9 | 3 |
| Pyrophosphate | .... | 6 |
| "Heptaphosphate" | .... | 6 |
| "Hexametaphosphate" | 24 | 6 |
| Maddrell's salt | 22 | 2 |

*Interference of Orthophosphates.* While the synergists protected to about the same degree in .01 molar borate buffers (pH 7.5) and in unbuffered solutions at the same pH, orthophosphate buffers interfered markedly with the antioxidant activity of the synergist studied and in the case of Maddrell's salt eliminated all antioxidant effect (Table III). Such interference might be expected if it is assumed that orthophosphates as well as citrate and polyphosphates can form complexes with the quinone. The molar concentration of the orthophosphate in the buffer is of course very much greater than that of the highly polymerized "hexametaphosphate" or sparingly soluble Maddrell's salt.

*Effect of Citrate and Polyphosphates at pH 5.4.* The results of several experiments at a lower pH are summarized in Table IV. The order and degree of effectiveness of synergists in unbuffered solutions at this pH are about the same as at pH 7.5, except that at the lower pH the trimer ($Na_3P_3O_9$) had no effect. It has been shown that in alkaline solution this compound may partially hydrolyze to $Na_5P_3O_{10}$ (2). This may be the reason for its antioxidant activity at the higher pH. Evidently hydrolysis of the polyphosphates to orthophosphates is not sufficient within the time of these experiments to interfere with their antioxidant activity.

In the presence of an acetate buffer the antioxidant activity of the most active metaphosphates, particularly Maddrell's salt, is considerably diminished. Whether this is due to more rapid hydrolysis in the presence of the buffer or to a direct interference by acetate similar to that noted with orthophosphates is not clear.

*Calcium Phosphates.* From a nutritive standpoint it would probably be preferable to use calcium rather than sodium salts as antioxidants in foods since calcium is one of the food essentials most likely to be inadequate in the American diet. For this reason the antioxidant activities on plain lard of several calcium pyro and metaphosphates were compared with the corresponding sodium salts. When adjusted to pH 7.5, neither calcium acid pyrophosphate ($CaH_2P_2O_7$) nor tetracalcium pyrophosphate ($Ca_2P_2O_7$) were quite as effective as the sodium salts. Calcium metaphosphate [$Ca(PO_3)_2$] had very little effect and monocalcium phosphate [$CaH_4(PO_4)_2$] none at all. Solubility of these salts is very limited; none were completely dissolved at the concentration of 0.1% used.

Since "hexametaphosphate" is known to form soluble complexes with calcium (the basis of its water softening action), the effect on antioxidant activity

TABLE IV

Antioxidant Effect of Citrate and Polyphosphates at pH 5.4 on Plain Lard

| Synergist (.1%) | Days to Turn Rancid | |
|---|---|---|
| | Lard No. 2 Acetate Buffer .01 Molar | Lard No. 2 Unbuffered |
| Control | 4 | 3.5 |
| Orthophosphate $(PO_4)^{3-}$ | 4 | .... |
| Metaphosphate, trimer $(P_3O_9)^{3-}$ | 4 | .... |
| Pyrophosphate $(P_2O_7)^{4-}$ | 11 | 9 |
| Triphosphate $(P_3O_{10})^{5-}$ | 10 | 10 |
| Citrate | 9 | 8 |
| "Heptaphosphate" $(P_7O_{22})^{9-}$ | 13 | 17 |
| "Hexametaphosphate" $(PO_3)^{n-}$ | 11 | 21 |
| Maddrell's salt $(NaPO_3)_x$ | 4.5 | 19 |

of addition of various amounts of calcium to a solution of this polymer was tried. However calcium caused a rapid fall in the pH of the "hexametaphosphate" solutions, indicating hydrolysis of the polymer, and greatly reduced its antioxidant effect.

*Effect of Citrate and Polyphosphates in Presence of Added Copper and Iron.* Since no special precautions were taken in these experiments to eliminate traces of copper or iron occurring in the distilled water, filter paper, etc., it was considered possible that the antioxidant activity of citrate and the polyphosphates might be due to a counteracting of the catalytic effect of trace metals. Both citrates (3) and polyphosphates (8, 16) are known to form complexes with metallic ions. Citric acid was shown to eliminate the pro-oxidant effect of small amounts of iron and copper added in the form of their stearates to dry vegetable fats (7).

The addition of 3 p.p.m. of copper in the form of copper sulfate to 0.1% solutions of several synergists caused acceleration in all cases (Table V). The synergists were all adjusted to pH 7.5. The control was a phosphate buffer at the same pH. None of the synergists eliminated the effect of the added copper under these conditions. However, especially with the polyphosphates, the antioxidant indices obtained in the presence of added copper were higher than without the copper.

The addition of ferric ions in the form of ferric chloride had very little effect on rancidity at pH 7.5 even at a concentration of 10 p.p.m. In the absence of citrate or polyphosphates, ferric hydroxide precipitated from the solution. At a concentration of 0.1% citrate or "hexametaphosphate" the iron was held in solution, but the pro-oxidant effect of the added iron was slight and irregular either with or without the synergists.

At pH 5.4, iron at a concentration of 4 p.p.m. had a pronounced accelerating effect on rancidity, both in the presence and absence of the synergists. Again the experiment does not furnish convincing evidence that these antioxidants act by inhibiting the catalytic effect of metals. It is still possible that they could counteract the effect of smaller amounts of metal (less than 1 p.p.m.) which might be present in the solutions. Evidence on this point is difficult to obtain. Redistillation of the water in all Pyrex stills did not make any difference in the rate of rancidification.

*Synergists in Dry Fats.* The activity of citrate and phosphates in dry lard did not parallel their antioxidant effect in aqueous fat systems. Phosphoric acid, completely ineffective in the presence of moisture, was an excellent antioxidant in the dry lard, even without added antioxidants. Neither metaphosphoric acid nor any of the polyphosphates tried gave significant protection in the dry fat, whether incorporated as finely powdered solid or mixed with the fat in the form of 50% solutions. In a typical experiment of this kind on plain lard, the control sample turned rancid in 10 days, various sodium salts of ortho, pyro, and metaphosphoric acid from 9 to 14 days, citric acid 17 days, and orthophosphoric acid 46 days, all in concentrations of 0.1% of the weight of fat.

Pyrophosphoric acid protected dry lard to about the same extent as orthophosphoric acid at the same concentration and had the added advantage of protecting also when the fat was brought into contact with buffer solutions.

## Discussion

It is apparent that there are great differences in the protective effect of the antioxidants studied in dry fats as compared to aqueous fat systems. The reasons for such differences are obscure. If, as Calkins has suggested, phenolic inhibitors form complexes with water soluble synergists as the first step in the synergistic mechanism, the relative solubility of such complexes in fat versus water becomes of importance. The complex may result in the synergist being drawn into the fat as postulated by Calkins. On the other hand, it might have the effect of drawing the phenolic inhibitor into the water.

Compounds of the formula $(NaPO_3)_x$ evidently cannot supply hydrogen to the quinone. If the quinone is reduced, the hydrogen must be derived ultimately from the fat rather than the synergist. The function of the synergist may be confined to the breaking of chain reactions by formation of addition compounds with activated unsaturated fats. Phosphorus pentoxide as well as phosphoric acid can add on to olefins (10) so that it does not seem essential that the synergists have labile hydrogens.

More information is needed on the effect of metals and metal complexing agents on rancidity in aqueous fat systems. No such agent has as yet been found which will eliminate or even greatly reduce the catalytic effect of added copper or iron in such systems.

Regardless of the mechanism of their antioxidant activity, the group of polyphosphates studied here in artificial systems seems to be sufficiently promising to warrant further investigation in foods where rancidity and associated oxidative changes are a problem, as in some cereal and baked products, meat products, fish, dairy products, fried foods, margarine, etc.

The polyphosphates are inexpensive as compared to other known synergists and unobjectionable in color, odor, and flavor. There would seem to be no reason to expect toxic effects from the soluble poly-

TABLE V

Effect of Added Copper and Iron on Antioxidant Activity of Various Synergists

| Synergist (.1%) | Days to Turn Rancid | | | |
|---|---|---|---|---|
| | Effect of Copper—pH 7.5 | | Effect of Iron—pH 5.4 | |
| | Control | 3 p.p.m. Cu | Control | 4 p.p.m. Iron |
| Control | 3 | 0.8 | 4 | 1.8 |
| Citrate | 6 | 2 | 12 | 6 |
| "Hexametaphosphate" | 19 | 8 | 20 | 12 |
| Maddrell's salt | 17 | 9 | 21 | 9 |

phosphates since they hydrolyze ultimately to orthophosphates. They have been used extensively as water softeners. The insoluble Maddrell's salt has been tested sufficiently to allow its use as an abrasive in tooth powders.

Their usefulness may be expected to be limited by several considerations: 1) Interference of orthophosphates and probably of other ions, 2) Hydrolysis of metaphosphates through pyro to orthophosphate. The hydrolysis is accelerated by heat, acid, and alkaline earth metals, particularly calcium in foods. In this connection it should be mentioned that solutions of "hexametaphosphate" and Maddrell's salt, adjusted to pH 7.5 were kept several months in a refrigerator without noticeable loss of antioxidant activity. Also these compounds showed high antioxidant activity in experiments with heated muscle extracts extending over many weeks at 45° (5).

## Summary and Conclusions

The antioxidant activities of a number of synergists were measured in aqueous fat systems at several pH values. A group of polyphosphates not previously investigated was most promising of the synergists tried. Orthophosphates were ineffective but antioxidant activity increased from pyrophosphate through tri and "heptaphosphate" and finally to the most active "hexametaphosphate" and Maddrell's salt. Citrate compared with triphosphate and pyrophosphate in antioxidant activity; all other synergists tried were less effective than pyrophosphate.

Relatively large molar concentrations of orthophosphates interfered markedly with the antioxidant activity of citrate and the higher polyphosphates.

The polyphosphates also inhibited rancidity in the presence of added copper and iron but did not eliminate the catalytic effect of the metals.

Antioxidant activity of the phosphates in dry fats did not parallel their activity in aqueous fat systems.

Properties of polyphosphates which might affect their use as antioxidants in foods are discussed.

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# Solvent Extraction. II. The Soaking Theory of Extraction[1]

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THE study of extraction of crude lipids from vegetable oil-bearing materials for application of the data to equipment design or process control makes apparent the need for a clearer understanding of the mechanism by which oil transfers from the solid to the liquid or miscella phase. In spite of the extensive application of solvent extraction, particularly in the soybean processing industry, there is no universally accepted concept of the manner in which the basic process occurs. The problem is reviewed briefly by Karnofsky (2). The present paper extends our knowledge of the subject but is not a complete answer.

Oil-bearing seeds that are usually prepared in the form of flakes or grits for the extraction process have a porous structure. King (1) has established the volumetric composition of a raw soybean flake to be 51% dry solid, 8% water, 22% oil, and 19% air. Where porous materials are being extracted, the theory of diffusion may be expected to apply, and the data should conform with theoretically derived equations for diffusion.

Extraction of soybean oil from porous clay plates does conform to theory as proved by Boucher (5). King demonstrated that data for the extraction of oil from soybean flakes fail to conform (1). Osborn (3) applied the concept of two parallel structures, one permitting fast extraction and the other slow, and obtained a better agreement with the diffusion theory. However the application of this concept to present data required the assumption of more than two structures. This involves complications that limit the usefulness of the concept in commercial design.

An oil-bearing substance such as a flake, is composed of four parts: 1. non-oil-bearing solids, 2. water, 3. oil, and 4. air space as illustrated in Figure I. For the purpose of this discussion the non-oil-bearing solids and water are treated as a single

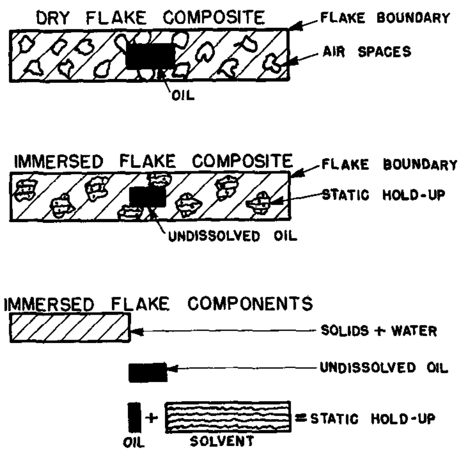

FIGURE I

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