Utilization of Phosphates in Meat Products

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Although it has been known since the work of Ellerkamp and Hannerland in 1952 that phosphates are very effective in increasing the functionality of processed meat products, they have not been used extensively in the U.S. In the last 12 months, however, the use of phosphates in meat products has increased rather dramatically due to two main reasons:

(1) As a result of pressure from consumer groups to reduce sodium levels in food products, many meat processors have turned to phosphates as partial replacements of sodium chloride.

(2) Recent changes in legislation have allowed the use of phosphates in a much larger range of meat products.

Although phosphates have been shown to be very effective in replacing salt in meat products (Bendall, 1954; Swift, 1957; Sherman, 1961; Shults et al., 1972; Pepper and Schmidt, 1975), they may have potential drawbacks themselves. At high concentrations (0.4% to 0.5%) they have an adverse effect on flavor, producing a metallic astringent flavor (Karmas, 1970: Ellinger, 1972). They may also contribute to possible health problems, both short term (abdominal distress and diarrhea) and long term (increased bone calcium mobilization) if used at the maximum permissible level (0.5%) (Bell et al., 1977). Potential problems associated with high salt and phosphate levels may be minimized by optimizing the combinations of phosphate type. phosphate concentration and salt concentration.

The general structure of the phosphates most commonly used in meat products is shown in Figure 1. Table 1 shows the correspondence between phosphate chain length and phosphate type. Phosphate types other than those listed in Table 1 that are permitted in meat products but are not widely used are: (1) the orthophosphates (monosodium phosphate and disodium phosphate) which are essentially orthophosphoric acid with either one or two of the three hydrogen ions replaced with sodium (2) the insoluble metaphosphates which are very long, straight chain phosphates, which have a chain length range of 100 to 500. The limited research that has been done with insoluble metaphosphates in meat products indicates that they are relatively ineffective (Bendall, 1954). Therefore, the discussion here will be restricted to the use of orthophosphates and the shorter chain length phosphates in meat products.

This review is to cover the utilization of phosphates in meat products. Due to the enormous array of meat product types and product composition, it is almost impossible to cover all products and give any of them justice. What is to be covered here is how phosphates affect functionality. From this information and some basic knowledge of the products, it will be possible to determine how phosphates can be used most effectively in each product.

Figure 1

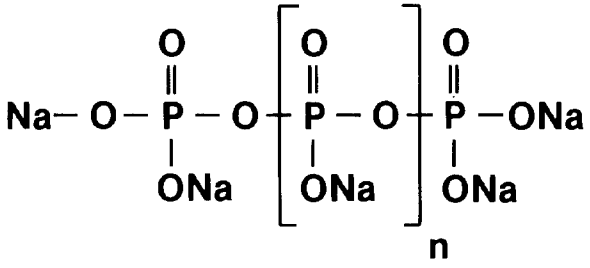

Figure 1. The general formula of straight chain phosphates.

Table 1. Nomenclature and Chain Length of Phosphates Commonly Used in Meat Products.

Name	*Abbr.*	*Chain length Range*[a]
Tetrasodium pyrophosphate	PP	2
Sodium tripolyphosphate	TPP	3
Sodium tetrapolyphosphate	TTPP	4-10
Sodium hexametaphosphate	HMP	10-15

a Ellinger 1972

Polyphosphates are known to increase both the amount of water bound and the strength of the meat particle-particle binding in processed meat products. The extent to which this occurs depends on the type and concentration of polyphosphate used and the concentration of other added salts (Trout and Schmidt, 1983; Shults et al., 1972). Much of the research that has been done in this area has been aimed at determining the mechanism by which phosphates increase waterholding capacity of meat, with little directed at

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meat particle binding. The literature reviewed here will mainly pertain to water binding capacity (WBC) but many of the ideas can be extrapolated to meat particle binding as these two parameters are highly correlated (R = 0.92, Trout and Schmidt, 1983; R = 0.64, Moore et al., 1976).

Water binding capacity, as referred to here, is a general term used to describe the extent to which water is held or bound by meat or meat products once cooked. It includes the more specific terms used in the literature, such as cook yield, cooking loss (inversely) and water binding value. It does not directly relate to the term "water holding capacity (WHC)," described by Hamm (1957), which is a measure of how much water is bound in the uncooked state.

Hamm (1960; 1970) summarized the effect of polyphosphates on the increase in WBC in meat products as being due to:

(a) An increase in pH.
(b) An increase in ionic strength.
(c) The ability to chelate divalent metal ions.
(d) The ability to bind to meat proteins.
(e) The ability to dissociate actomyosin.

The relative importance of each of these properties is not well known as it is difficult to separate the individual effects without modifying the whole system. But it is known that some of these properties (particularly pH and ionic strength) individually contribute to increases in WBC. Much of this discussion will pertain to changes that occur in the myofibrillar proteins as they contain 70% of the water in muscle (Hamm, 1960). But this does not preclude the role of other proteins in water binding, as during processing and subsequent heat treatment the water initially associated with the myofibrillar proteins can translocate. Once this occurs, the water binding ability of the other meat proteins may become important.

The Effect of pH

Increasing the pH of meat from 4.0 to 7.0 results in a progressive increase in WBC (Hamm, 1970). The small pH increase produced by phosphates, 0.1 to 0.3 pH units depending on phosphate type and concentration (Ranken, 1976), is only expected to produce a small increase in WBC (Hellendoorn, 1962; Hamm, 1970). More recent research has shown that: (a) the pH increases in uncooked products are much greater than the pH increases reported for cooked products (Trout and Schmidt, 1983); (b) relatively small changes in pH of the uncooked products containing salt and phosphate have a pronounced effect on WBC (Puolanne and Matikkala, 1980).

When investigating the effect of phosphate type and concentration on functionality of restructured meat products, Trout and Schmidt (1983) found that the increases in pH of the uncooked products ranged from 0.1 to 0.7. They also found that the pH increase of the cooked product was similar to previously reported values (0.05 to 0.3 pH units). Puolanne and Matikkala (1980) found that changes in uncooked product pH had the greatest effect in the pH range 5.4 to 6.1. This was the case with wieners prepared with 2.0% salt, both with and without the addition of 0.3% phosphate. Hence, phosphates that can increase the pH of meat products to the upper limits of this range will be most effective in increasing WBC.

The Effect of Ionic Strength

Increasing the ionic strength of a meat system increases the WBC (Hellendoorn, 1962). However the increase in ionic strength produced by phosphates is difficult to measure, due to the fact that phosphates are not completely dissociated in solution (Van Wazer, 1960). It was only recently that a concerted effort was made to determine the extent of dissociation of different phosphate types at the concentrations used in meat products. Trout (1983) determined the degree of dissociation of 6 different phosphates whose chain length varied from 1 to 22. He found that with increasing phosphate chain length there was a concurrent reduction in the degree of dissociation. When the ionic strength of a 0.5% phosphate solution is computed, taking the degree of dissociation into consideration, there is a reduction in ionic strength with increasing phosphate chain length (from 0.2 to 0.09) over the chain length range investigated. This is in contrast to the results obtained when the degree of dissociation is not included in the calculations, where there is an increase in ionic strength (from 0.21 to 0.60) with increasing chain length over the same chain length range. The lower ionic strength of the longer chain length phosphates may explain the results of Shults et al. (1972). They found that hexametaphosphate (with a chain length of 12-14) was less effective than pyrophosphate and tripolyphosphate in increasing WBC.

The increase in WBC produced by increases in ionic strength has been found to occur over a relatively narrow ionic strength range. The work of Mahon (1961), Hellendoorn (1962), Isiorishi et al. (1979), and Trout and Schmidt (1983) has shown that the increase in WBC (both with and without phosphate) begins when the total ionic strength is $\simeq$0.4 and continues until the ionic strength $\simeq$0.6. Although none of the phosphates can increase ionic strength to this extent, it does indicate that they will be most effective when used in conjunction with 1% to 2% salt. This is in agreement with experimentally obtained results (Gillett et al., 1978; Puolanne and Ruusunen, 1980).

Chelation of Divalent Cations

The ability of polyphosphates to chelate metal ions, particularly calcium and magnesium ions, was postulated by Hamm (1960) as being an important factor in increasing the WBC of meat. His theory was that magnesium and calcium ions bind to proteins, causing tightening of the molecular network structure and release of water. Hence, if these ions could be removed by chelating compounds, then WBC would increase. This theory was refuted by: (1) Inklaar (1967), who demonstrated that polyphosphates did not reduce the amount of protein bound calcium or magnesium ions; (2) Hellendoorn (1962), who did not find any increase in WBC by the addition of the chelating agents EDTA or oxalate. From this it must be concluded that chelation of calcium and magnesium ions is not a major factor in the increase of WBC produced by phosphates.

Binding to Meat Proteins

The binding of phosphate anions to meat proteins, to either specific binding sites as occur in actomyosin or to non-

specific positively charged protein side groups, has been postulated as an explanation for the increase in WBC. Phosphate binding results in an increase in the net negative charge of the protein, which in turn leads to greater protein-protein repulsion and consequently to increased WBC (Hamm, 1970).

Naus et al. (1968) have shown that myosin bound two moles of pyrophosphate per mole of myosin, but actomyosin bound only one mole. From this they concluded that each myosin molecule had two phosphate binding sites, but that one site was made unavailable due to the binding of actin. One point which tends to reduce the possible role of this type of binding in WBC is that it is independent of ionic strength in the range 0.1 to 0.6. In this ionic strength range, the increase in WBC produced by phosphates increases with increasing ionic strength (Hellendoorn, 1962; Bendall, 1954).

The non-site specific binding of phosphates to meat proteins, as occurs with other proteins, may be important in increasing the WBC. A point in its favor is that all types of phosphates bind to proteins, but to varying degrees depending on the phosphate type and the particular protein (Lyons and Siebenthal, 1966; Vandegrift and Evans, 1981). This type of binding is helpful in explaining why the different phosphate types are effective in increasing WBC, but to varying degrees. The extent of binding may determine the degree to which the WBC is increased. However, von Hippel and Schleich (1969) have stated that in fibrous proteins the conformational changes associated with the presence of phosphate ions are not due to the binding of the ions to the proteins. This conclusion was based on the findings that phosphates altered the conformational stability of native and acetylated collagen to the same extent, even though phosphates cannot bind to acetylated collagen.

Dissociation of Actomyosin

The increase in WBC produced by the presence of pyrophosphate was suggested by Bendall (1954) as being due to the increased solubility of muscle proteins as a result of the pyrophosphate-induced dissociation of actomyosin. A prerequisite for this dissociation is the presence of low levels of magnesium ions. These ions bind to the myosin molecule and in so doing allow the pyrophosphate ions to bind to myosin. Once pyrophosphate is bound, it dissociates actomyosin into actin and myosin with a subsequent release of orthophosphate (Granicher and Portzehl, 1964).

This ability to dissociate actomyosin is a property of pyrophosphate and not tripolyphosphate, but both phosphates increase WBC similarly (Hamm, 1970). According to Yasui et al. (1964), tripolyphosphate is dephosphorylized to pyrophosphate by a phosphatase activity present in the myofibrils. Hydrolysis of tripolyphosphate has been observed in both actomyosin (Tonumura et al., 1967; Hamm and Neraal, 1977) and meat homogenates (de Mann, 1973).

Although this appears to be a possible explanation for the effect of phosphates in meat products, it does have some shortcomings. Phosphates other than pyrophosphate have been shown to be very effective in increasing WBC. It has been shown that orthophosphate (Seman et al., 1980), tripolyphosphate (Shults et al., 1972) and tetrapolyphosphate and hexametaphosphate (Trout and Schmidt, 1983), are all effective in increasing WBC. In the study by Trout and Schmidt, it was shown that when changes in ionic strength and pH were taken into consideration there was no difference in effectiveness of pyrophosphate, tripolyphosphate, tetrapolyphosphate and hexametaphosphate.

It may be argued that the effectiveness of tripolyphosphate is due to being hydrolyzed to pyrophosphate which is then the effective ion. If this is the case, then the effectiveness of tripolyphosphate will be dependent on the time dependent hydrolysis. The studies by Ranken (1976), Poulanne and Ruusunen (1980) and Trout and Schmidt (1983) have shown that increasing the amount of time from preparation to thermal processing had no effect on the WBC of meat products containing tripolyphosphate.

The original research that indicated that pyrophosphate was more effective than salt of a comparable ionic strength and pH was carried out by Bendall (1954). In that research, titration curves were used to determine the degree of dissociation of sodium acid pyrophosphate ($Na_2H_2P_2O_7$) and from that information the ionic strength was calculated. This is not a very accurate method of determining the degree of dissociation and hence the ionic strength. The ionic strength calculated by Bendall for a 0.5% pyrophosphate solution was 0.11. Since then it has been shown, using conductance measurements (Van Wazer, 1960) and sodium ion electrode measurements (Trout, 1983), that the ionic strength of a 0.5% pyrophosphate solution is between 0.19 and 0.20. When Bendall's original data is recalculated based on this information, it is found that there is no significant difference ($P>0.05$) between the phosphate and salt treatments at the same ionic strength and pH. A similar error in ionic strength calculation was made by Hellendoorn (1962) in arriving at a similar conclusion to Bendall's.

The Role of Ionic Strength and pH

From the preceding discussion, it may be concluded that increases in ionic strength and pH produced by phosphates are the most important properties in determining WBC. To reinforce this concept, Trout and Schmidt (1983) have studied the effect of varying phosphate type (pyrophosphate, tripolyphosphate, tetrapolyphosphate and hexametaphosphate), phosphate concentration and salt concentration on WBC. They found that, irrespective of phosphate type or concentration, maximum WBC was obtained when the pH was greater than 6.0 (the uncooked pH) and the total ionic strength was greater than 0.6. The total ionic strength used included the ionic strength contribution of the meat $\approx$0.26 (Dubuisson, 1950).

This is in good agreement with the work of Yasui et al. (1980) and Samejima et al. (1981). These workers have studied the effect of pH and ionic strength (using potassium and sodium chlorides) on the gel strengths of actomyosin, myosin and myosin fragments. They concluded that the strength of these protein gels is determined by ionic strength and pH with the maximum effect occurring at pH 6.0 and an ionic strength of 0.6. The effect of pH and ionic strength was found to be cooperative in nature and associated with the αhelix-random coil transition of the rod portion of myosin. Using scanning electron microscopy, they have shown that the maximum gel strength occurred when the helical rod

portion of myosin underwent a transition that resulted in the formation of a characteristic three-dimensional lattice structure. Siegel and Schmidt (1979) found that this same type of structure occurs with both myosin and actomyosin in the presence of salt and tripolyphosphate, but not when these salts were absent. The extent of WBC and binding seems to be dependent on the production of this characteristic three-dimensional lattice structure. This type of structure is effective in entrapping water within its lattice structure and is much stronger than other similar structures that can form.

Summary

The properties of phosphates that are most important in increasing the WBC of meat products are their ability to increase ionic strength and pH. WBC increases with increasing ionic strength and pH until the total ionic strength is greater than 0.6 and the pH of the uncooked product is greater than 6.0. Hence disodium phosphate, tetrasodium pyrophosphate and sodium tripolyphosphate, which are the most effective phosphates in increasing ionic strength and pH, will increase WBC to the greatest extent. On a molecular scale, WBC seems to be determined by the production of a characteristic three-dimensional lattice structure. This is the result of the unfolding of the αhelical rod portion of myosin. Due to the lack of supporting evidence, the role of chelation of divalent cations, dissociation of actomyosin and binding of phosphate ions in increasing WBC must be considered as pure postulation — at least until evidence can be presented for their importance.

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