PHOSPHORUS COMPOUNDS IN LEATHER INDUSTRY

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The possible applications of phosphorus compounds in leather-making are reviewed. Polyphosphoric acid or its salts are used as (a) pretanning agent in vegetable tanning and (b) pretanning or retanning agent or complexing component in chrome tanning. Polyphosphates are also water softeners. The phospho-compound tetrakis (hydroxy methyl) phosphonium chloride is a good tanning agent in the presence of resorcinol. Phosphatides and alkyl phospho-esters are complexing lubricants. Chrome complexes of alkyl phospho-esters are waterproofing agents. Phospho-acrylates are good additives to acrylic finishes for imparting flame-proof characteristics. Polyfluoro alkyl phosphates impart oil repellent characteristics to leathers. Triaryl phosphates are good plasticisers for vinyl and cellulosic finishes; they are also flame-retardents.

Phosphorus products e.g. articles made out of bone, the mineral turquoise etc., had been used as articles by primitive men. Since the early beginning, application of phosphorus products for a variety of utility purposes has made great strides. Agriculture industry is the major consumer of phosphorus as phosphatic fertiliser and animal feed. There are very many other applications for phosphorus compounds, both organic and inorganic[1] eg, tricalcium phosphate is used as pigment extender; triaryl phosphates like tricresyl phosphate are used as plasticisers in coating formulations.

In the leather industry the most commonly used phospho-compounds are polyphosphates which are used as auxiliary tanning agents for altering the characteristics of variously tanned leathers. Other phospho-compounds that are used or could be used in leather-making are (a) tetrakis (hydroxy methyl) phosphonium chloride as tanning agent, preferably in combination with a phenol; (b) phosphatides as lubricant, (c) alkyl phospho-esters of long-chain alcohols as complexing lubricant or water-proofing compound, (d) phospho acrylic and other phosphorus compounds as flame proof leather finishes and (e) florophosphates as oil repellent compounds.

Polyphosphates as auxiliary tanning agent[2-18]

Water soluble polyphosphates like tripolyphosphate (eg. $Na_5P_3O_{10}$) are used in leather making.

Lindner[2] of Germany and Wilson[3] of United States independently discovered

that polyphosphates can tan hides and skins and the earlier work on chemistry and technology of application of polyphosphate as auxiliary tanning agent was well documented.[4]

As pretanning of collagen with polyphosphate reduces the fixation of vegetable tannins[4,5] and the deamination of collagen reduces the fixation of polyphosphate,[4,5,6] it was considered that polyphosphate takes position between peptide chains of collagen and combines with them to some extent when polyphosphate and amino groups of collagen are facing each other.[4,7,8] The involvement of amino sites of collagen in polyphosphate tanning is evident by the fact that skin tanned with polyphosphate has less affinity to acid.[4]

Polyphosphate pretannage for vegetable leather[2-11]

Polyphosphate pretannage protects the surface of the leather, particularly the grain, from too rapid fixation of vegetable tannins especially when strong vegetable tan liquors are used in tanning.[9]

Polyphosphate pretreatment, hence, is well suited for "rapid floatless processing" of hides and skins with vegetable tanning extract powders as well as for the processes wherein the skins come into contact directly with strong vegetable tan liquors[10,11] as the pretreatment avoids the possible case hardening or drawn grain due to rapid excessive fixation of vegetable tannins on leather surface.[9] This advantage alone may not be sufficient ground for adoption of polyphosphate pretanning for vegetable tanning in view of high cost, but saving of tanning time and labour by the adoption of rapid vegetable tanning processes using vegetable tanning extract powder or strong liquors coupled with uniform colour and physical properties such as high tensile strength and grain elasticity[9] makes the polyphosphate pretreatment a commercial proposition. The improvement in colour is due to strong sequestering action of poly-phosphates on iron and calcium;[9] during polyphosphate pretannage iron stains and calcium that might have been deposited as calcium carbonate causing "lime blast effect" are removed; the hides and skins are thus rendered free of these defects. As salts especially chlorides adversely effect the combination of polyphosphates with collagen, delimed hides and skins are washed well until these were salt free and they were treated with polyphosphates in acidic pH of 2.2-2.3, since maximum absorption takes place at this pH.[9] As this pH is too low to the vegetable tannage the polyphosphate tanned leathers are thoroughly washed prior to vegetable tanning.

Polyphosphate treatment in chrome leather making[2,4,12-19]

Polyphosphates can be used in the manufacture of chrome tanned leather either before or after chrome tannage and occasionally also during tannage.

Usual feed stock for chrome tanning with basic chrome salts is pickled hides and skins as the pickling adjusts the pH of the skin and the degree of swelling. If the difference in pH of the feed stock and acidic chrome tanning salts is high, then there will be excessive fixation or precipitation of chrome on the surface of

hides and skins resulting in drawn grained leather. The classical pickle treatment can be replaced by treatment with non-swelling acids, like polyphosphoric acids. The benefit of such pre-treatment is smoothness and tightness of grain. The pre-treatment also contributes to a more rapid uptake and uniform distribution of chrome throughout the cross section of the pelt. A part of the polyphosphate present in the pretanned stock may complex with chrome. As the phosphate pre-treatment is done on delimed stock, it is to be noted that the feed stock cannot be bated with pancreatic bate which requires just alkaline conditions for its activity but can be bated with fungal bate which is active at acidic pH.[16]

8–9% of P_2O_5 can be incorporated in chrome tanned leather by retreating the chrome tanned leather with polyphosphates without causing grain cracking.[17] The treatment with sodium polyphosphates neutralises the chrome leather throughout the cross section of the leather being treated whereas carbonate treatment acts only on the surface. Chrome leather thus treated has tight grain and better appearance because iron impurity, if any, present in the leather is complexed.

Though polyphosphate can be used in the chrome tanning bath itself, this procedure is seldom practised since precipitation may result if proper care is not taken. With chrome alum dissolved in cold or with aged diluted 33% basic chrome solution polyphosphate gives precipitate which dissolves in excess polyphosphate due to the formation of non-cationic chrome complexes which have no tanning action. Freshly prepared chrome alum of 0 or 33% basicity does not precipitate with polyphosphate because of sulphate masking which renders the liquor aniomic. Hence if polyphosphate is to be added in the chrome tanning bath then solid chrome extract should be applied to the feed stock along with the phosphate and diluted after penetration of chrome into the leather; or freshly prepared chrome liquor should be treated with other masking agents like formate first and then with phosphate eg. chrome liquor masked with ¼ mole formate can be further masked with ¼ mole of phosphate without any difficulty. The tannage is not done in pickle bath but in a separate bath.[18]

As the masking with polyphosphate reduces the cationic charge the affinity of such leather to anionic dye and anionic fatliquors is decreased and affinity to cationic dye or cationic fatliquor is increased,[12,17,18] while the anionic fatliquor used in lubricating leather is necessarily less.[17]

Tetrakis (hydroxy methyl) phosphonium chloride as tanning agent[17,24]

Tetrakis (hydroxy methyl) phosphonium chloride (THPC) $[(HOCH_2)_4 P^+Cl^-]$ can be used alone in tanning of hides and skins,[19,20] but leather was thin and firm. A new tanning process was developed wherein THPC and resorcinol were applied to skin under mildly alkaline condition so that they react *in situ* in the pelt and develop a compound which tans collagen;[20-23] the leather has good hydrothermal stability (T_s>95°C). The mode of tannage is to treat the pelt being depickled with resorcinol 2.5% and THPC 4.5% (percentages are on pickled weight)

and to raise the pH of the tanning bath slowly by the addition of a mild alkali Combination tanned leather obtained by pretanning with THPC + Resorcinol and retanning with chrome was reported to possess not only good hydro thermal stability but also good sweat resistance.[23,24] Leather tanned with THPC and resorcinol alone is full, round and mellow and has many properties similar to those of vegetable tanned leathers. It is suggested that the reaction product of THPC and resorcinol forms amino ethyl linkage with ε amino group of the lysine residue of collagen. The strong covalent forces of this linkage were considered to be the reason for high hydrothermal stability of THPC tanned leathers;[23] it should be noted that resorcinol itself will also combine with collagen.

Phospho-compounds as leather lubricants

Phosphatides: One of the earliest applications of phospho-compounds in leather making was the application of phospho-lipids for converting putriscible hides and skins into leather. Pre-historic man rubbed the brain of the animal he killed to the hide or skin of the animal for making it imputriscible. So that it would not decay on exposure to moist weather condition. The brain is rich in phosphatides, so also the egg yolk. Egg yolk is a good fatliquor.[25] It contains roughly 50% water, 16% protein, 30% fat out of which 3% is phosphatide and the rest other matters like sugars. The phosphatide of egg yolk is bound to the chrome tanned leather because of its ability to complex with chrome. The fatliquoring composition containing egg yolk is considered to be ideal for leathers like hunting suedes as it imparts dry feel which is beneficial in improving the nap of the leather. The ability of egg yolk to impart dry feel to the leathers is also the reason for its incorporation in certain fatliquoring compositions for glazed kid. Instead of egg yolk, lecithin obtained from other sources is at times used in fatliquoring compositions.

Alkyl phospho-esters as complexing lubricant or waterproofing agent[26-29]

The present trend is to lubricate upper leathers such that leather has minimum free oil and maximum bound oil as the higher percentage of free oil will impair the adhesion of upper to synthetic sole during vulcanising. The impairment of adhesion is due to migration of free oil at the vulcanising condition to the leather surface. Use of fatliquoring compositions containing complexing lubricant is recommended for lubricating vulcanisable chrome leather.[28] Fatliquoring compositions containing complexing lubricant are also considered to be well suited for dry cleanable leathers. The complexing lubricant as the very name indicates, complexes with chrome leather and hence is firmly bound to the leather; they do not migrate to the surface of leather during vulcanising or do not get dislodged due to dry cleaning. Alkyl phospho-esters like mono phosphoric esters [$ROPO(OH)_2$] eg., mono dodecyl orthophosphate are used as complexing lubricant component of the fatliquoring compositions. The fatliquors containing complexing lubricants are called as "complexing fatliquor". Complexing fatliquors may contain 10-20 parts of complexing lubricant, 40-50 parts of sulphated oil and the rest may be raw

and mineral oil; fatliquoring compositions having no raw and mineral oil are also used.

Complexing phospho lubricants like mono dodecyl orthophosphates if used alone, i.e. not in the presence of sulphated oils after complexing with chrome render the leather water/showerproof because of protruding lengthy alkyl chain.

But to use them as waterproofing agents they have to be applied in the form of sodium or ammonium salts. Such application, however, may make the grain surface of chrome leather coarse because of pH effect. Hence application of chrome complexes of alkylated phospho-esters in water dilutable alcoholic solvents is advocated for imparting showerproof characteristics to chrome leather. The phospho-chrome complexes are more stable than chrome fatty acid complexes which are used for similar purposes; the better stability of phospho-chrome complexes is due to the better ability of phosphates to complex with chrome as compared to carboxyl.

Leathers, vegetable or chrome, can also be made waterproof by incorporating surface active phosphatic emulsifiers like condensation product of mono lauryl acid phosphate and ethylene or propylene oxide or amine salts of alkyl amide derivatives of mono alkyl acid phosphate. The surface active agents are incorporated into leathers in non-polar solvents. They will swell within the leather on contacting with a small quantity of water, fill the void space in the leather and effectively prevent further uptake of water by the leather.

Phospho-compounds in leather finishes[30,31]

Acrylic products as emulsion and solution polymer are widely used in leather finishing as the leather treated with the product has good wet rub resistance. These products generally have poor heat and flame resistance. This deficiency of acrylic finishes can be overcome by incorporating thermosetting flame proofing characteristics; addition of a copolymer of dialkyl phosphono alkyl acrylate and methacrylate and vinylidene compounds,[30] in acrylic top coat may serve this purpose.

Alternatively finished leather surface can be made to have flame proof character by applying phospho-compounds like N-diethyl-amino-phosphoric acid diamide[31] in water or solvent phase either alone or along with other phospho-compounds like phospho-acrylics.

Phospho-compounds as oil repellents[32]

Polyfluoro alkyl phosphates having medium alkyl chain length can be applied to leather for imparting oil repellent characteristics to leather.[32] Products of this type may find place in industrial gloves and garments. Oil and soil repellency will be very much appreciated in garments; soil repellency can be achieved by treating the leather with fluoro silicones[33,34]

Phospho-compounds as plasticisers

Triaryl phosphates like tricresyl phosphates $(CH_3C_6H_4)_3\ PO_4$, are used as plasticisers for vinyl and cellulosic leather finishing agents eg. N.C. lacquers. They also serve the purpose of flame retardent.[1]

Other miscellaneous applications

Polyphosphates are good water softeners as they are good sequestrants for calcium and magnesium present[1] in hard water, but they are seldom used for that purpose by the leather industry in view of high cost.

Phosphorus penta sulphide and other polysulphides eg. those obtained by reacting 8 mol or more of sodium sulphide with 1 mol of phosphorus penta sulphide alone or along with sodium thio phosphate are recommended for use as unhairing agent;[35,36,37] the cost of the product/s is an inhibitive factor for the commercialisation of this class of unhairing agent.

The possible application of phosphorus compounds in production of leather is reviewed; it is hoped that this review may catalyse newer approach of application of phospho-compounds for improving the quality of leathers.

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