

Selecting a Sequestering Agent

– More than a Complex?

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Water is an important ingredient in the recipes of textile wet processing. Due to inadequate availability of good-quality surface water, many units are compelled to use ground water. The quality of ground water is not always as good as surface water, and it could contain soluble calcium and magnesium salts, leading to hardness.

This hardness can be corrected by using a water softening plant, which can remove these metal salts and replace them with sodium salts, but these softening plants may not take care of other metal salts of Cu^{2+} , Ni^{2+} , Fe^{3+} , Cr^{3+} , etc, if present in raw water, and these metal salts can cause problems in textile wet processing.

Even though water is softened, unwanted metal salts can creep in from one or more sources, as mentioned below:

- a) Basic raw material – Mineral content of cotton, which varies from region to region, or higher iron content of raw water.
- b) Metal contamination during storage and transport of other ingredients such as Mild Steel drums used for dyes and chemicals. Basic chemical like caustic lye being transported in Mild Steel tankers or MS drums.
- c) Poor quality of piping used for water from the softening plant to the dye house.
- d) Rust during spinning, weaving or handling of the substrate.
- e) Iron contamination from machine parts such as joints, bolts, etc, which are made from non-specified material.

Thus, even if soft water is used for processing, some problems due to metal impurities can crop up unexpectedly, leading to value loss or reprocessing and putting pressure on thin margins.

Let us review situations where metal impurities can create problem.

1. In the scouring of cotton, particularly package yarn and terry towel, the presence of calcium and magnesium leads to insoluble salt deposition on the substrate, leading to harsh feel and/or resist marks. Also, scale formation on continuous bleaching ranges and package dyeing machines could take place due to presence of calcium.
2. In the bleaching of cotton with peroxide, pinhole marks in fabric and hosiery, lower tensile strength in the case of yarn, and poor spinnability of bleached cotton fibre are the result of iron and copper impurities. Sometimes, pinhole marks may not be seen but DP values would be lower, though whiteness remains the same. Also, the presence of calcium can rapidly decompose hydrogen peroxide.
3. In reactive dyeing, precipitation of dyestuff could take place due to the presence of calcium, leading to dye spots and poor colour yield, and affecting reproducibility.
4. In washing off of reactive dyestuffs, poor wash fastness and wet rub fastness result from the presence of calcium.
5. In the case vat and sulphur dyes also, the presence of calcium reduces fastness properties.
6. In the case of disperse dyes, the presence of calcium may lead to agglomeration due to the formation of calcium salt, with anionic dispersing agent present in commercial disperse dyes.

7. Certain anthraquinone disperse dyes, blues, reds pinks and red violets, form a complex with Cu^{2+} , Fe^{3+} , Ni^{2+} , Co^{2+} present in traces. The blue dyes precipitate and other dyes change tone to a dull, bluish shade.
8. In dyeing wool with chrome dyes, premature precipitation before chroming could take place and lead to poor rubbing fastness.
9. Direct dyes, which are used in a few markets, can also lead to precipitation in the presence of Cr^{3+} , Ni^{2+} , Cu^{2+} , Co^{2+} if the dyestuff has specific groups in its structure.

Thus, unwanted metal salts cause a lot of problems in processing. Now, with the focus on minimising costs and maximising efficiency, consistency and fastness are two important parameters that every dyer would like to achieve first time. This reduces reprocessing costs, making him competitive.

The dyer has to use a suitable sequestering agent in the process, wherever it is required. Selection of the right sequestering agent is very important. First and foremost, the sequestering agent should chelate offending metal ions under the given condition and should form a stable complex, which does not decompose over a prolonged processing period.

Selective chelation is also critical. For example, in peroxide bleaching of cotton, calcium and iron has to be complexed, but not magnesium, since magnesium ions act as a stabiliser for peroxide. If the chelating agent chelates magnesium also, then the addition of magnesium chloride is advisable, to stabilise the bath.

Another example is the desizing of cotton fabric by the enzymatic pad-batch or pad-steam method. Many customers try to remove iron impurities during desizing, to avoid pinhole marks during subsequent scouring/bleaching. A sequestering agent added during desizing should preferentially chelate iron and not calcium, as calcium acts as a stabiliser for enzymes.

In dyeing with metallised reactive or direct dyes containing metal ions, the sequestering agent should not demetallise the dyestuff, i.e. remove metal ions from dye molecules, which will lead to shade change.

Let us review the chemistry of various types of sequestering agents and the conditions under which these are most effective.

Sequestering agents work by a mechanism of complex formation, also termed chelation. The sequestering/chelating agent has groups at appropriate locations in the molecule to form one or more chelate rings with the metal ion. The complex thus formed remains soluble as well as stable under given conditions. These

Figure 1 EDTA calcium complex

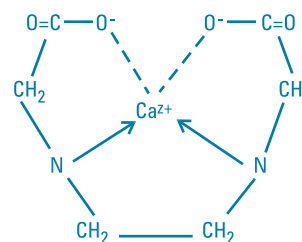


Figure 2 Tetra sodium salt of EDTA

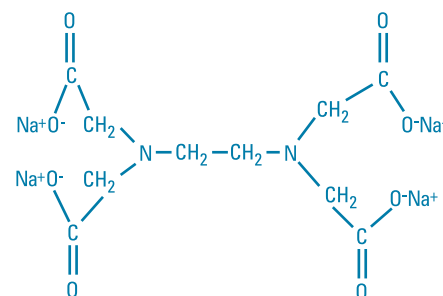


Figure 3 Nitrilo triacetic acid sodium salt (NTA)

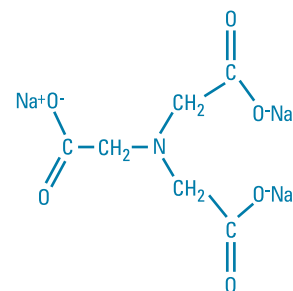


Figure 4 Diethylene triaminepentaacetic acid sodium salt (DTPA)

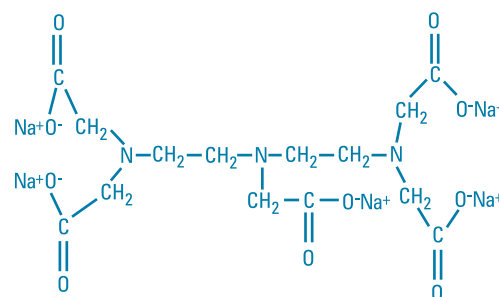
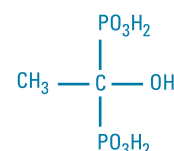


Figure 5 1 - Hydroxy ethylidene - 1,1 - diphosphonic acid (HEDP)



chemicals usually contain nitrogen, such as amines and substituted amines, and oxygen in the form of carboxyl, phosphate or hydroxy groups. (see Figure 1)

The three main types of commercial sequestering agents are:

- Aminocarboxylic acid based products
- Phosphates & Phosphonates
- Hydroxy carboxylates
- Polyacrylates
- Sugar acrylates

Aminolcarboxylates

In aminopolycarboxylates, (Figures 2 to 4) it is assumed that one molecule of sequestering agent complexes with one ion of metal. Depending upon the pH of the medium, i.e. acidic, neutral or alkaline, the preferential sequestering order for each product could change. For example, NTA has shown the following preferential sequence at different pH.

Acidic medium = $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$

NTA Neutral medium = $\text{Cu}^{2+} > \text{Fe}^{3+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$

Alkaline medium = $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$

Some of the characteristics of some of these sequestering agents are summarised as below.

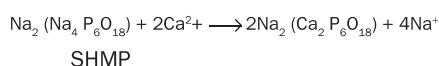
- * EDTA – Good sequestering agent for calcium and magnesium at alkaline pH but no sequestering action on Fe^{3+} at alkaline pH. Not stable with oxidising agents. Low solubility in acidic medium.
- * NTA – Sequestering of Fe^{3+} only at acidic pH but sequestering of Cu^{2+} between pH 3 to 12. Low solubility in acidic medium. Not stable with oxidising agents.
- * DTPA – Good sequestering action on Fe^{3+} under alkaline pH but complexes with alkaline earth salts are less stable than EDTA. Slightly more resistant to oxidising agents. Low solubility in acidic medium.

Phosphates & Phosphonates

These sequestering agents are divided in two broad classes:

- Inorganic polyphosphates such as sodium hexameta phosphate (SHMP), sodium polyphosphate, sodium tripolyphosphate, sodium trimeta phosphate, sodium pyrophosphates
- Phosphonated aminopolycarboxylates such as EDTMP, DETMP, ATMP, HEDP, DTPMP

Inorganic phosphates work under specific conditions and work as sequestering agents by converting troublesome metal ions into water-soluble complexes by a process of ion exchange.



But such complexes are not stable under high temperature and break down to simple phosphates, which cannot retain metal ions in complex form. For example, a complex of calcium, SHMP, which is shown here, is transformed to insoluble calcium orthophosphate on prolonged boiling.

Phosphates of aminopolycarboxylic acids or phosphonates are derivatives of phosphorous acid (H_3PO_3) and are characterised by a C-P bond, which has stronger hydrolytic stability than the P-O-P bond of polyphosphates. This type of sequestering agent has emerged as a major class of sequestering agent, since these possess more features than mere chelation. These characteristics are:

- Threshold effect, i.e. inhibition of precipitation of CaCO_3 , CaSO_4 with sub-stoichiometric quantities of inhibitor
- Corrosion inhibition
- Resistance to hydrolysis
- Deflocculation, i.e. stability effect on colloidal suspensions

The structures of the important commercial products are shown in Figures 5 to 7. Compared to popular amino polycarboxylic acid-based sequestering agents, these phosphonate-based sequestering agents have a high chelation ratio. Table 1, shown above, gives a comparison of the chelation value as expressed in mg of CaCO_3 /gm of 100% sequestering agent in acid form, and chelation ratio as moles of CaCO_3 chelated per mole of sequestering agent at pH12.

Apart from better chelation value or better chelation ratio, these phosphonates also have better iron chelation than EDTA and NTA.

Hydroxy carboxylic acids

Organic compounds that have several hydroxylic groups often have the property of preventing precipitation of bi- and trivalent metal cationis in an alkaline medium. Some of the well-known products in this category are:

Citric acid, Tartaric acid, Gluconic acid and Oxalic acid shown in Figures 8 to 11

These are less important sequestering agents, compared to aminocarboxylic acid or phosphonates. Gluconic acid/sodium gluconate has been found to be an effective chelating agent for iron under alkaline conditions.

Polyacrylates

Polyacrylates are effective dispersants, with mild chelation values and protective colloid properties. The chelation values of polyacrylates have no demetallising effect on metal-containing dyestuffs. They are completely non-foaming (see Figures 12).

Table 1

Product	Mol. Wt.	Chelation Value at				Chelation Ratio
		pH9	pH10	pH11	pH12	
HEDP	206	830	860	860	870	1.80
ATMP	299	725	890	1030	1050	3.10
EDTMP	436	1070	1170	1170	1150	5.01
DTPMP	573	920	1130	1170	1230	7.05
EDTA	292	370	360	350	355	1.03
NTA	191	510	500	515	515	0.98

Figure 6 Aminotrimethylenephosphonic acid (ATMP)

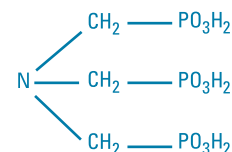


Figure 7 Diethylene triaminepentamethylene phosphonic acid (DTPMP)

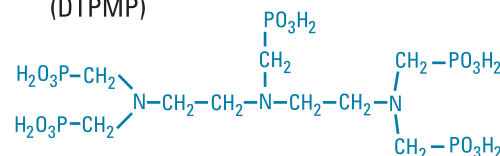


Figure 8 Citric acid

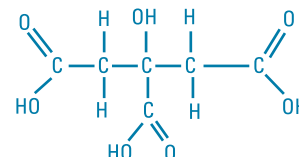


Figure 9 Tartaric acid

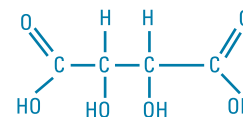


Figure 10 Gluconic acid

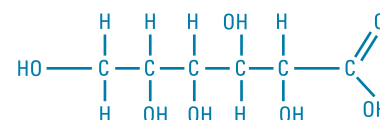


Figure 11 Oxalic acid

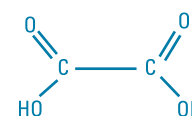


Figure 12 Polyacrylate

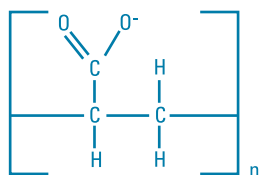


Figure 13 Gluconate

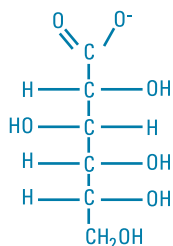
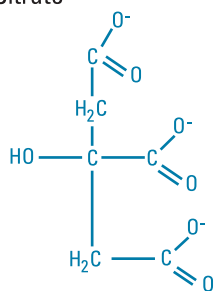


Figure 14 Citrate



They are very suitable as dyebath conditioners, soaping agents and washing aids. Being non surface-active agents they are easily rinsable and thus reduce the quantity of water required for removing their traces from the substrates, unlike all surfactants. The typical chelation values offered by polyacrylates do not come close to the chelation values offered by amino polycarboxylates or the phosphonates. This problem has been overcome by development of Sugar Acrylates.

Sugar Acrylates

Sugar Acrylates have sequestering values as high as amino polycarboxylates or the phosphonates. They are biodegradable, effective components in cellulosic fabric pretreatment during desizing, scouring, bleaching and mercerising. These products are characterised by good chelation values from the acidic to the alkaline range and from temperatures of 45 to 115°C. They also exhibit no demetallising effect on metal-containing dyestuffs and are non-foaming. They are ideally recommended in pretreatment for desizing, scouring and bleaching and as dyebath conditioners during the cellulosic dyeing.

Factors to be taken into consideration while selecting a sequestering agent for the process

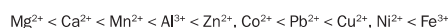
1. Stability constant – As chelation is a reversible reaction, the equilibrium is dependent on the process pH and the concentration of the metal ions and chelating agent, which react together to form a chelate. The stability of the metal complex is expressed in terms of its stability constant. If we represent chelation of metal ion, M^{m+} with sequestering agent, A^{n-} , as: $M^{m+} + A^{n-} \rightleftharpoons MA^{(m-n)}$

then the stability constant is

$$K_s = \frac{MA^{(m-n)}}{[M^{m+}][A^{n-}]}$$

A high value of K_s indicates high sequestering effect. For example, in the case of aminopolycarboxylates, the stability constant for same metal iron increases in the order $NTA < EDTA < DTPA$.

In the case of metal ions, the stability constant increases in the order.



From the above information it can be deduced that the $NTA-Mg^{2+}$ complex has the least stability, whereas $DTPA-Fe^{3+}$ has the highest stability. Thus, in a process, if more than one metal ion is present, the metal ion having the highest stability will be chelated preferentially. If chelating agent is present in sufficient quantity, the metal with the highest stability constant will be chelated completely, followed by the next metal ion, in the order given above. Even after chelation is complete in this order, if additional metal impurity, with metal having a higher stability constant, is introduced, then this metal ion will displace low-stability-constant metal ions from the complex. For example, Fe^{3+} displaces Ca^{2+} from a Ca^{2+} – chelating agent complex. Of course, the chelating agent should be capable of chelating Fe^{3+} under given conditions.

- 2. The pH of the process** – the pH of the system will influence the formation of the chelation complex. For example, NTA, EDTA cannot chelate Fe^{3+} under alkaline conditions, whereas DTPA can. HEDP can chelate Fe^{3+} up to pH 12, and so also gluconic acid.
- 3. Demetallisation** – This property is particularly important for dyeing and printing with premetallised dyes – for example, some direct, reactive and premetallised metal complex dyes. If Ni^{2+} , Cu^{2+} , Cr^{3+} , Co^{2+} or Fe^{3+} is present in premetallised dyes, these could be preferentially chelated ahead of Ca^{2+} and Mg^{2+} , due to the higher stability constant of these metal ions. Therefore pretrials in the

lab are required to establish the suitability of the chelating agent, and also to arrive at the optimum concentration for the given process, when premetallised dyes are to be used.

- 4. Other features** – stability of chelate to prolonged process periods, dispersing properties, crystal-growth inhibition, effect on equipment, etc – are also to be considered when selecting a commercial sequestering agent.

Thus, defining the requirement of a chelating agent and screening the available products in the lab can avoid many unpleasant surprises or accidents in processing.

Understanding these fundamentals, we at Sarex-Supertex have developed a number of formulations for textile processing, which are described briefly here.

- 1. Saraquest 2UD** – For chelation of iron during desizing, peroxide bleaching and acid demineralising, without affecting any other parameters.
- 2. Saraquest AE** – For chelation of calcium and iron during peroxide bleaching, for improved stability and whiteness, to produce full white.
- 3. Sarakol PS /1583** – For preferential chelation of calcium in reactive dyeing and reactive washing off, to improve consistency of dyeing as well as improve fastness properties. It does not have any demetallising effect on metal-containing dyes.
- 4. Saraquest W** – For dyeing of reactivities where water hardness is more than 200 ppm. This product also does not have demetallising effect on metal-containing dyes when used at the required concentration.
- 5. Sarastabil-MRS** – A bleach bath stabiliser and sequestrant, having the capacity to chelate alkaline earth metals Ca^{2+} , Mg^{2+} and Fe^{2+} and Cu^{2+} under highly alkaline conditions. ○