

Complex Problems Can Have Sugary Solutions

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THE QUALITY of water used in the textile finishing industry plays a significant part. In addition to undesired excess consumption of textile auxiliaries and dyestuffs, water hardness can cause disruption to processes, and incrustations on the textile substrate, on the machines and pipes, resulting into inferior final fabric quality.

In the textile industry, a 'sequestering' agent is understood, in the broader sense, to mean an auxiliary chemical that forms a complex with metals such as iron, copper, nickel, zinc and magnesium, which are present in water and affect the textile processing in many way.

The alkali builders, or sequestering agents, or chelating agents, used for this process deactivate the water-hardening substances and other harmful cations in the water by precipitation, ion exchange, chelating or adsorption on the seed-crystal surface. These agents bind polyvalent cations such as calcium and magnesium in water and in fibres, thus preventing the precipitation of soaps. If polyvalent ions are present, insoluble soaps may form, settle on the fabric and produce resist spots. Even if the process water is softened before the liquor formulation, the addition of a sequestering agent brings certain clear advantages in respect of the reliability of the process.

As the amount of additives can vary considerably, depending on the origin of the cotton and its past history (in some cases up to 2 or 3 times the average values), it is becoming increasingly difficult for those carrying out the pretreatment to guarantee the uniform, reproducible quality of the fabric prepared for dyeing, printing or finishing.

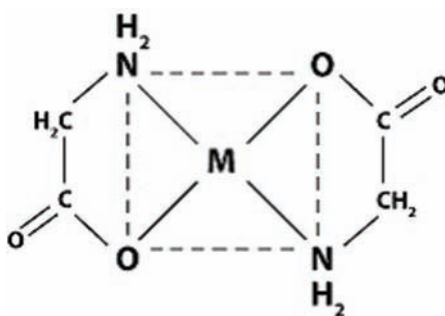
Mechanism of Chelate Formation

In the case of sequestration, a polyvalent cation is tightly surrounded as a 'central atom' by other oppositely charged ions or by neutral molecules, known as ligands. Ligands must be able to supply at least one non-binding electron pair and the central cation must have a number of

empty orbitals of a suitable energy level to accommodate these electron pairs. A ligand that is only able to supply one electron pair is referred to as a monodentate. The number of monodentate ligands that are able to be grouped around the central ion determines the co-ordination number of the relevant ion.

For a chelate to form, it is necessary to have a ligand that can supply at least two pairs of electrons, which are sufficiently far apart from each other in the ligand molecule to be able to form a bridge. This type of ligand is a bidentate or a ligand with two co-ordinate bonds. The majority of sequestering agents are polydentates with 4-8 co-ordinate

bonds. The chelates usually contain 2 moles of ligand (glycine) and one mole of metal, as demonstrated in the following figure:



Conventional Sequestering Agents: Effects and Side-Effects

There are five major types of sequestering agent to choose from¹:

1. Inorganic polyphosphates
2. Aminocarboxylic acids
3. Organophosphonic acids
4. Hydroxycarboxylic acids
5. Polyacrylates

There are a number of alternative products on the market, which claim to be as effective as Ethylenediamine tetraacetic acid (EDTA) or Nitrili triacetic acid sodium salt (NTA), but most also have their restrictions. For example, the **inorganic polyphosphates**, such as sodium tripolyphosphate, sodium hexametaphosphate, sodium polyphosphate, sodium trimetaphosphate and sodium

pyrophosphate, are probably the best overall, in that, in addition to sequestering most metals, they also aid in cleansing the fibres. They may, however, hydrolyse at high temperature and lose their effectiveness.

The **aminocarboxylic acid** type sequestering agents, such as EDTA, NTA and DTPA (Diethylene triaminepentacetic acid sodium salt) are very good in that they sequester most metal ions and are very stable under alkaline conditions. But generally they are not stable to oxidising agents and have limited solubility in acidic medium. These are the most-used types.

The **organophosphonic acid** types, such as ethylenediaminetetra (methylene phosphonic acid), DETMP, ATMP, HEDP, are also very effective but comparatively expensive. Also, complexes are not stable under high temperature and break down to simple phosphates, which cannot retain metal ions in complex form.

Oxalates and **hydroxycarboxylic acids** (citrates, Tartaric acid, Gluconic acid, Oxalic acid, etc) are excellent for sequestering iron under alkaline condition but not effective for calcium and magnesium. In order to quickly and effectively bring the chemicals to the textile material, i.e. to improve their wettability and to ensure that the fibrous impurities will be removed as far as possible, it is necessary to add surfactants with good wetting and washing/emulsifying properties.

In the case of **polyacrylates**, though they have no demineralising effect on metal-containing dyestuffs and are effective dispersants, they offers low chelation values as compared to the chelation values offered by amino polycarboxylates or the phosphonates.

The potential applications for sequestering agents in wet textile processes of all types are diverse. The presence of the metals during bleaching or dyeing can result in pinhole marks, reduced brightness efficiencies, change in shade or reduced depth. Metals can also contribute to brightness reversion, either during the bleaching process or while the finished material is stored. It has therefore been difficult to find a good

solution that matches the performance profile of traditional chelating agents.

Also, from an ecological point of view, the use of this group of substances must be reduced, as the phosphate load is one of the most significant contributing factors for the eutrophication of ground water. Therefore, the search for a cost effective alternative to the two most frequently used chelating agents, NTA and EDTA, has long been an industry target. Any alternative has to possess a good ecological and toxicological profile – and we can also add a third requirement: that the product should largely be made from renewable sources. This problem has been overcome by the development of sugar acrylates.

Sugar Acrylates

Sugar acrylates, or sugar acrylic polymers, are synthesised by polymerisation of acrylic acid in presence of enolisable sugar under alkaline condition. They have sequestering values as high as amino polycarboxylates or the phosphonates and are biodegradable. Sugar acrylates 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 de-metallising 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 cellulosic dyeing.

To meet stringent 'green' requirements, Sarex has developed a biodegradable, sugar-acrylate-base sequestering agent, Chelatin SA. It is a direct alternative to NTA and EDTA, fulfilling all of the targets set above.

Efficiency Evaluation

The evaluation of the efficiency of a chelating agent may be based on the number of different chemical and physical measures, which are generally affected by the variables such as ionic strength, pH, method of measurement, temperature, etc. Hence, a study to evaluate the chelating agent Chelatin SA was carried out to assess its binding capacity with respect to metals such as calcium, copper and iron, over wide range of pH. Also, as a practical-application study, disperse and reactive dyeing was carried out to observe the change in shade, depth of dyeing and dispersion properties.

Evaluation of Binding Capacity

Calcium Chelation Power:

Normally, calcium-chelation values are determined at room temperature. Due to

diverse application of sequestering agents in textile wet processing, Chelatin SA has been tested over a wide range of pH values, ranging from 4 to 12, for its calcium-binding capacity (See Figure 1). From the experimentation, it has been observed that the calcium-binding power of Chelatin SA increases with the increase in pH from 4 to 10, giving chelation values in the range of 49.47 to 255.16 respectively, which slightly decreases with increase in pH above the pH value of 10.

Iron Chelation Power:

Iron-binding capacity is nothing but the iron-hydroxide dissolution capacity of the sequestering agent. The binding capacity of Chelatin SA was tested at room temperature at various pH values, ranging from 5 to 12. Figure 2 shows the minimum and maximum values of iron chelation, ranging from 60 to 240 for pH 5 to 12 respectively. From the measured data it is clear that the capacity for dissolving a significant amount of iron from the precipitated hydroxide goes on increasing with increase in pH and is maximum at pH value 12.

Copper Chelation Power:

In the case of the copper binding power of Chelatin SA, the same trend is observed as was observed earlier in the case of iron-binding power. Here also, copper-binding capacity increases with increase in pH, which is maximum at pH 12, showing a maximum copper-binding power of 240 (See Figure 3).

From the study of the binding power of Chelatin SA, carried out over a wide pH range, it is clear that Chelatin SA achieves very good chelation power at various pH values, especially from pH 10-12.

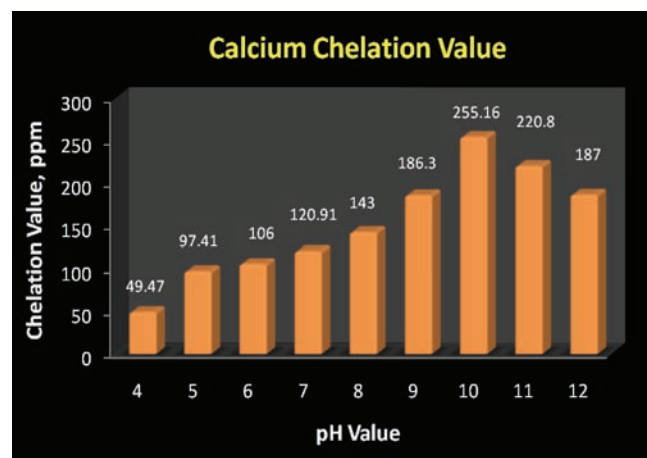


Figure 1: Calcium Binding Capacity of Chelatin SA

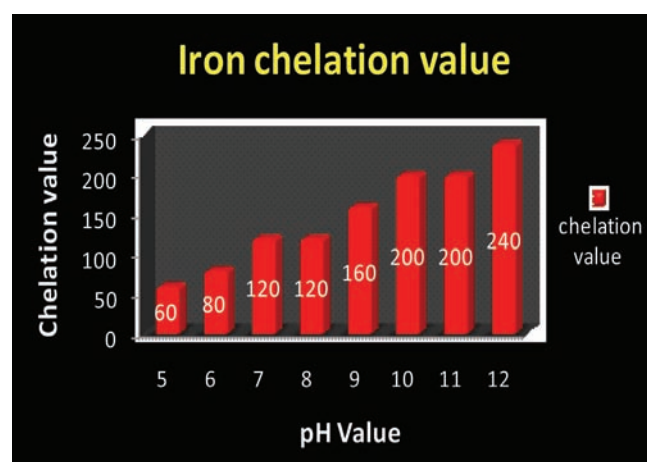


Figure 2: Iron Binding Capacity of Chelatin SA

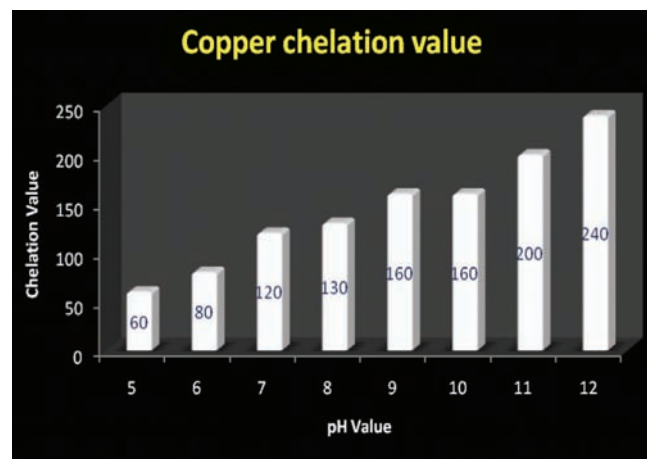
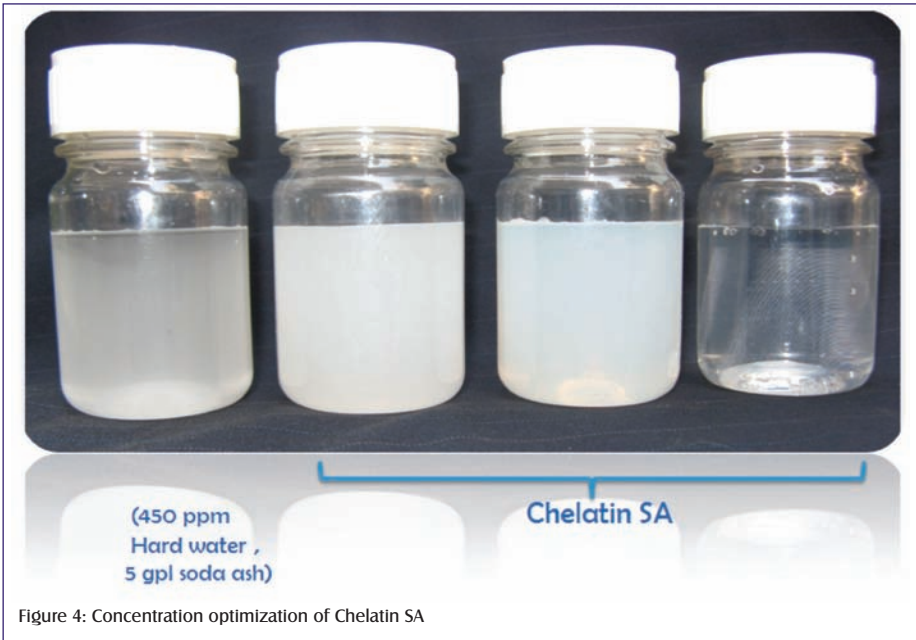


Figure 3: Copper Binding Capacity of Chelatin SA

Application Study of Chelatin SA

As discussed earlier, although Chelatin SA shows very good binding power, in order to judge its practical viability, a study of dyeability with respect to disperse and reactive dyeing was carried out in hard water.

The basic experiment was carried out to optimise the concentration of sequestering agent to chelate the water of hardness 450ppm containing 5g/l soda ash (See Figure 4). From the figure it is clear that 3g/l Chelatin SA is required



to chelate 450ppm hard water and to make it free from metal impurities, to avoid further processing difficulties.

A study of the effect of Chelatin SA was carried out in **disperse dyeing** by using 100ppm iron and 6ppm copper separately in the dyebath (See Figure 5: A and B). From the figure, it is crystal clear that a change in shade of polyester is observed when dyed in a bath containing 100ppm iron and 15ppm copper. No shade change of comparable depth is observed in a polyester dyed with 2 and 3g/l Chelatin SA respectively. Thus, Chelatin SA proves to have very good iron and copper binding power in acidic medium.

Also, to prove the dispersing power of Chelatin SA, a **dyeability study with reactive dye** on cotton was carried out in the presence of 50ppm and 70ppm of copper and iron separately, with and without 2g/l Chelatin SA. After dyeing, dye remainder was collected in test tubes and kept separately (See Figure 6). After 10 minutes, the remainder was observed for any settlement. Settlement was observed in test tubes a, b, c, f, g and h, which contained copper and iron with no Chelatin SA, indicating poor dispersing power. The dyebath remainder in test tubes d, e, i and j, containing copper and iron with the sequestering agent Chelatin SA, showed no settlement, indicating very good dispersing power, which will not allow the precipitate to settle on the substrate during the dyeing process.

Conclusion

The above results shows that Chelatin SA has very good chelation and disperse capacity and is capable of replacing conventional polyacrylates and even phosphonates in textile applications. It forms stable complexes with problem metals, 'tying-up' their reactive sites. Also, Chelatin SA is effective during desizing, scouring, bleaching and dyeing. It prevents the individual ions from reacting with the dye and reducing efficiency. The stable chelant/metal ion complex, or chelate, can be subsequently washed-off during further processing.

From this it is clear that Chelatin SA can fulfil the requirements of industry as an alternative, 'green' sequestering agent. ID

Reference:

1. "Selecting Sequestering Agent – More Than a Complex", Dr. Naresh M. Saraf and Mr. Deepak V. Alat, *International Dyer*, June 2004.

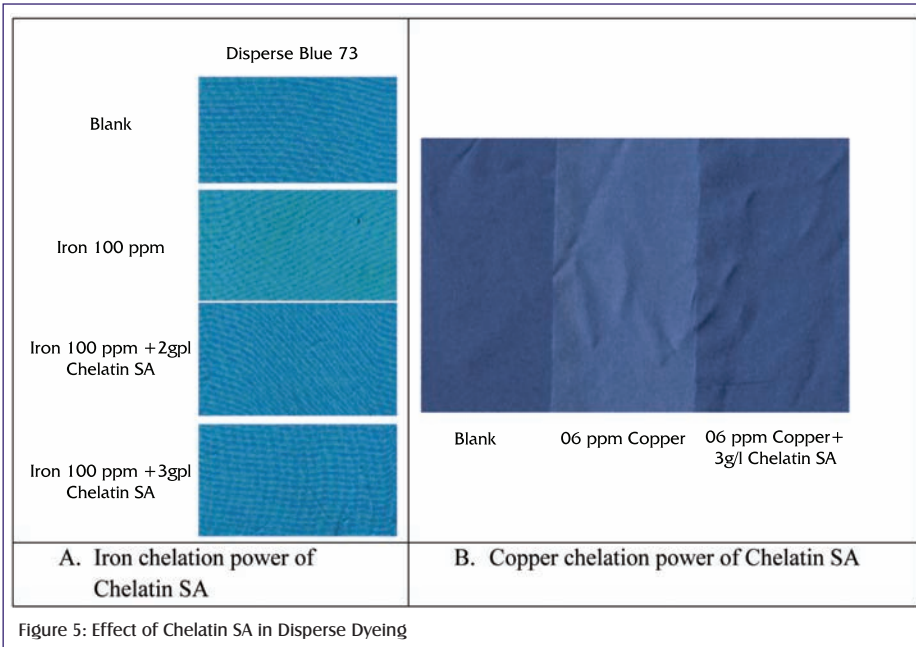


Figure 5: Effect of Chelatin SA in Disperse Dyeing

