# Six Blind Men and an Elephant – The Story of Stabiliser

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## PART I
## Evaluation of Stabilisers

Bleaching of cotton is carried out to convert naturally occurring pigments to colourless form by oxidation. Among the various oxidizing agents available, ie. Sodium/Calcium hypochloride, Hydrogen Peroxide, Sodium Chlorite, Sodium/Potassium persulphate, Hydrogen Peroxide is the most popular bleaching agent for continuous and discontinuous process.

The active bleaching component in bleaching with Hydrogen Peroxide is Perhydroxyl ion

$$H_2O_2 \longrightarrow HOO^- + H^+$$

The mechanism of bleaching and various possible reactions during bleaching have been postulated but none of them yet scientifically proved.

The commercial Hydrogen Peroxide is available at acidic pH (pH 4.5 – 5.0) to make it stable during transportation and storage, whereas peroxide bleaching for cotton is carried out traditionally at alkaline pH (pH 10.5 – 11.0). In bleaching, the alkali works as an activator for Hydrogen Peroxide. It is a well-known fact that high alkalinity and high temperature accelerate Hydrogen Peroxide bleaching, leading to rapid decomposition of Hydrogen Peroxide. With a current trend of optimizing processes and reducing cost, combined scouring and bleaching of cotton for Dyers White (RFD) and Bleachers White (Full White) is very common and popular among the dyehouses processing cotton in any form. Some adventurous dyers also carry out combined scouring and bleaching at 110°C and the more adventurous at 130°C! Under such conditions of high alkaline pH of 14.0 and temperature above 100°C, to control bleaching is a very tough task. For such operations, we need products, which will slow down decomposition of Hydrogen Peroxide, so that the maximum quantity of Hydrogen Peroxide is available for bleaching, and this will also prevent oxidative damage to cotton. These products are termed as Stabilisers and are supposed to work in exactly the opposite way to activators. Sodium Silicate was the first such stabiliser, used successfully for peroxide bleaching. But the problem of silicaceous deposits on fabric and equipment led to the search for better stabilisers. Also, in developing countries, transportation and storage of sodium silicate is done in MS containers, leading to iron contamination, which is much more dangerous than silicaceous deposits.

Magnesium ions present in hard water, as well as present in cotton, were found to have a stabilising effect in peroxide bleaching. Some enterprising suppliers also tried to sell preparations of magnesium salts as Stabilisers! Even today, some of the MNCs sell formulations of stabilisers containing magnesium.

Apart from these types, there is whole new range of peroxide stabilisers available today, which are based on organic compounds and are free from magnesium as well as silicate. Like the mechanism of Hydrogen Peroxide bleaching, the exact mechanism of peroxide stabilisation is not yet proved. It is assumed that a buffering action and sequestering action on iron (III) and copper (II) could be a possible mechanism.

Since the exact mechanism of peroxide stabilisation is not known, it is difficult to compare different compounds or formulations for their efficiency in peroxide stabilisation by a simple analytical method. The only reliable method available to us is to carry out peroxide bleaching along with a substrate under identical conditions and measure the rate of decomposition of Hydrogen Peroxide over a period of time in the presence of different stabilisers at recommended dosage. Various lab experiments proved that peroxide bleaching with a substrate gives more accurate and realistic results than peroxide bleaching without substrate in comparison of stabilisers. Apart from the kinetics of peroxide decomposition and measuring residual peroxide at the end of bleaching, we also studied other parameters such as Whiteness Index, Yellowness Index, Sequestering action, and qualitative analysis for oxidative damage, to understand more about stabilisers.

Experimental details are given below.

## EXPERIMENTAL DETAILS

**Material –** Grey cotton hosiery, single Jersey 40s (most popular quality) obtained from bulk production, made from the same yarn lot to avoid variation in mineral content and pigment content

**Equipment –** Rotadyer with 150ml capacity beakers, heating rate controller

Stabilisers used for study:

**Sarastabil MRS –** An economical organic stabiliser, silicate free and magnesium free

**Sarastabil M Conc –** An economical organic stabiliser, silicate free and magnesium free but with better stability to higher concentrations of alkali and peroxide used for continuous bleaching

**Saraquest AE –** A demineralising agent with good sequestering action on $Ca^{+2}$ & $Fe^{+3}$

**Saraquest W –** A high-power sequestering agent for $Ca^{+2}$ and $Fe^{+3}$ especially under alkaline pH and high temperature

**Saraquest 2UD –** Sequestering agent for $Fe^{+3}$ under alkaline conditions

We carried out combined scouring and bleaching of grey cotton knits with Standard recipes for Dyers White (RFD). The recipe was initially standardised in the lab for reproducible and consistent results. Details are given in *Table 1*. Experiments were carried out using distilled water. We also evaluated chelation values of stabilisers for $Ca^{+2}$ and $Fe^{+3}$ by using Standard procedures. Results are given in *Table 2*.

To study the efficiency of stabilisers in sequestering $Ca^{+2}$ & $Fe^{+3}$ under actual conditions, we purposely added $Ca^{+2}$, $Fe^{+3}$ and a combination of $Ca^{+2}$ & $Fe^{+3}$ to the Standard combined scour/bleach recipe with distilled water and evaluated the kinetics of bleaching and residual peroxide at the end of bleaching (*Table 3-6*). The same results are also exhibited in graphical form, *Fig.1-4, see page 32.*

Evaluation of scoured and bleached cotton knits in all experiments for oxidative damage was carried out by qualitative test and results are given in *Table 7*.

We also used LR grade Magnesium Chloride to check whether $Mg^{+2}$ ions can have any stabilising action on peroxide. The results are given in respective tables (*Table 3-6*).

## Results & Discussions

In combined scouring and bleaching for RFD, $MgCl_2$ when increased from 0.4g/l to 2g/l showed improved stabilisation effect. But at this concentration the possibility of formation of Mg $(OH)_2$ on the substrate is high. Other organic stabilisers showed good stability action equivalent to 2g/l $MgCl_2$ at very low dosage. Among all the stabilisers studied, Saraquest W showed the best performance at lowest concentration. We also observed that, with an increase in concentration at Saraquest W to 0.3g/l, overstabilisation takes place, leading to underbleaching. The excellent performance of Saraquest W can be attributed to highest chelation value for $Ca^{+2}$ & $Fe^{+3}$ under alkaline conditions.

### Table 1

| Recipe for Dyers White (RFD) |
|---|
| $H_2O_2$ (50%) : 3% |
| NaOH : 2% |
| Saradet NEW : 1% |
| Stabiliser : As per details given |
| MLR = 1:10, Temperature: 95°C, Time: 45 min. |

### Table 2

CHELATION VALUE:

| Sr. No. | Parameters | Product | | | | |
|---|---|---|---|---|---|---|
| | | Saraquest W | Saraquest 2UD | Saraquest AE | Sarastabil MRS | Sarastabil M Conc |
| 1 | $Ca^{2++}$ Chelation at room temp. at pH 12.5 – 13.0 | 430.0 | 82.5 | 89.0 | 38.1 | 90.4 |
| 2 | $Ca^{2++}$ Chelation at 60°C at pH 12.5 – 13.0 | 352.8 | 40.9 | 48.8 | 25.5 | 71.6 |
| 3 | $Ca^{2++}$ Chelation at 95°C temp. at pH 12.5 – 13.0 | 272.8 | 21.9 | 30.4 | 7.5 | 35.2 |
| 4 | $Fe^{3++}$ Chelation at pH 5.0 at room temp. | 240.0 | 180.0 | 60.0 | 40.0 | 80.0 |
| 5 | $Fe^{3++}$ Chelation at pH 12.0 at room temp. | 480.0 | 220.0 | 112.0 | 80.0 | 180.0 |

### Table 3

Combined scouring/bleaching of grey cotton knits in distilled water.

| Sr. No. | Products | % Residual $H_2O_2$ | | | | |
|---|---|---|---|---|---|---|
| | | Initial | 0 min. | 15 min. | 30 min. | 45 min. |
| 1 | Blank (without stabiliser) | 100 | 65.8 | 40.8 | 26.3 | 19.7 |
| 2 | $MgCl_2$ (0.4 g/l) | 100 | 68.8 | 46.3 | 31.3 | 20.0 |
| 3 | $MgCl_2$ (2.0 g/l) | 100 | 70.1 | 48.1 | 33.8 | 28.6 |
| 4 | Sarastabil MRS (0.3 g/l) | 100 | 74.4 | 52.4 | 34.1 | 24.4 |
| 5 | Sarastabil M Conc (0.1 g/l) | 100 | 73.2 | 52.4 | 35.4 | 24.4 |
| 6 | Saraquest W (0.1 g/l) | 100 | 72.8 | 53.1 | 42.0 | 32.1 |
| 7 | Saraquest W (0.3 g/l) | 100 | 72.0 | 61.0 | 53.7 | 46.3 |
| 8 | Saraquest AE (0.15 g/l) | 100 | 70.5 | 52.6 | 37.2 | 30.8 |
| 9 | Saraquest 2UD (0.3 g/l) | 100 | 65.8 | 48.1 | 35.4 | 25.3 |

### Table 4

Combined scouring & bleaching of grey cotton knits in presence of 220ppm Calcium chloride (80ppm $Ca^{+2}$)

| Sr. No. | Products | % Residual $H_2O_2$ | | | | |
|---|---|---|---|---|---|---|
| | | Initial | 0 min. | 15 min. | 30 min. | 45 min. |
| 1 | Blank (without stabiliser) | 100 | 62.5 | 38.8 | 26.3 | 16.3 |
| 2 | $MgCl_2$ (0.4 g/l) | 100 | 60.5 | 34.6 | 22.2 | 12.3 |
| 3 | Sarastabil MRS (0.3 g/l) | 100 | 67.0 | 43.9 | 29.3 | 20.7 |
| 4 | Sarastabil M Conc (0.1 g/l) | 100 | 67.9 | 43.2 | 30.9 | 22.2 |
| 5 | Saraquest W (0.1 g/l) | 100 | 71.6 | 50.6 | 37.0 | 28.4 |
| 6 | Saraquest AE (0.15 g/l) | 100 | 65.0 | 41.3 | 27.5 | 20.0 |
| 7 | Saraquest 2UD (0.3 g/l) | 100 | 65.0 | 38.8 | 26.3 | 17.5 |

## Table 5

Combined scouring & bleaching of grey cotton knits in presence of 10ppm Ferric Chloride (3ppm $Fe^{+3}$) :

| Sr. No. | Products | % Residual $H_2O_2$ | | | | |
|---|---|---|---|---|---|---|
| | | Initial | 0 min. | 15 min. | 30 min. | 45 min. |
| 1 | Blank | 100 | 56.3 | 34.5 | 21.8 | 13.8 |
| 2 | $MgCl_2$ (0.4 g/l) | 100 | 61.4 | 37.5 | 18.2 | 10.2 |
| 3 | Sarastabil MRS (0.3 g/l) | 100 | 60.9 | 40.2 | 27.6 | 21.8 |
| 4 | Sarastabil M Conc (0.1 g/l) | 100 | 65.9 | 39.6 | 27.5 | 23.1 |
| 5 | Saraquest W (0.1 g/l) | 100 | 59.8 | 41.4 | 27.6 | 23.0 |
| 6 | Saraquest AE (0.15 g/l) | 100 | 64.4 | 38.9 | 23.3 | 20.0 |
| 7 | Saraquest 2UD (0.3 g/l) | 100 | 65.9 | 42.0 | 22.7 | 20.5 |

## Table 6

Combined scouring and bleaching of grey cotton knits in presence of 80ppm $Ca^{+2}$ + 3ppm $Fe^{+3}$

| Sr. No. | Products | % Residual $H_2O_2$ | | | | |
|---|---|---|---|---|---|---|
| | | Initial | 0 min. | 15 min. | 30 min. | 45 min. |
| 1 | Blank | 100 | 56.0 | 33.0 | 11.0 | 6.6 |
| 2 | $MgCl_2$ (0.4 g/l) | 100 | 52.8 | 28.1 | 13.5 | 5.6 |
| 3 | Sarastabil MRS (0.3 g/l) | 100 | 63.7 | 38.5 | 24.2 | 17.6 |
| 4 | Sarastabil M Conc (0.1 g/l) | 100 | 63.7 | 39.6 | 25.3 | 19.8 |
| 5 | Saraquest W (0.1 g/l) | 100 | 60.4 | 42.9 | 28.6 | 20.9 |
| 6 | Saraquest AE (0.15 g/l) | 100 | 59.3 | 36.3 | 20.9 | 15.4 |
| 7 | Saraquest 2UD (0.3 g/l) | 100 | 61.5 | 37.4 | 22.0 | 16.5 |

(Note: For Table 3-6, Initial reading corresponds to reading taken at room temperature when the bath is prepared; whereas 0 min. reading corresponds to reading taken at 95°C as soon as temperature reaches 95°C.)

## Table 7

Qualitative Test for presence of oxycellulose (Methylene blue absorption test)

| Products | RFD in distilled water | RFD in presence of $Ca^{+2}$ 80ppm | RFD in presence of $Fe^{+3}$ (3ppm) | RFD in presence of $Ca^{+2}$ + $Fe^{+3}$ |
|---|---|---|---|---|
| Blank | Absent | Absent | Present | Present |
| Magnesium Chloride (0.4 g/l) | Absent | Absent | Present | Present |
| Sarastabil MRS (0.3 g/l) | Absent | Absent | Absent | Absent |
| Sarastabil M Conc (0.1 g/l) | Absent | Absent | Absent | Absent |
| Saraquest W (0.1 g/l) | Absent | Absent | Absent | Absent |
| Saraquest AE (0.15 g/l) | Absent | Absent | Absent | Absent |
| Saraquest 2UD (0.3 g/l) | Absent | Absent | Absent | Absent |

But chelation value cannot be considered the only feature in stabilising efficiency. If we compare the stabilising efficiency of Saraquest AE and Saraquest M Conc at equal concentration, Saraquest AE showed better performance than Saraquest M, though the $Fe^{+3}$ chelation value of Saraquest AE is lower than Saraquest M Conc. On the other hand, if we consider the performance of Saraquest 2UD, which has much better $Fe^{+3}$ chelation value than both Saraquest AE and Saraquest M Conc, the peroxide stabilising action of Saraquest 2UD, even at higher concentration than Saraquest AE and Saraquest M Conc, is not better than either of the products when these stabilisers are used in distilled water.

(*Fig. 1, see page 32,, Table 3*).

When the above experiments were carried out in distilled water with an addition of 80ppm $Ca^{+2}$, to create artificial hardness, we noticed rapid decomposition of peroxide without stabiliser and, surprisingly, $MgCl_2$ at 0.4g/l did not show any stabilising action. This means that under calcium hardness, $Mg^{+2}$ ions do not exhibit any stabilising action.

Other organic stabilisers showed lower performance than that with distilled water but residual peroxide was found to be around 20-28% at the end at 45 min. bleaching, indicating the required stabilising action. Saraquest 2UD showed low stabilisation under calcium hardness, which could be explained from its low calcium chelation values under alkaline condition (*Table 4, Fig. 2, see page 32*).

When the above experiment was repeated by the addition of 10ppm $FeCl_3$ in place of $CaCl_2$, we observed that, under this condition, $MgCl_2$ also failed to exhibit any stabilising action. Under this condition, all organic stabilisers showed the required stabilising action, even in presence of 10ppm $FeCl_3$. This experiment did demonstrate that even a small quantity of $FeCl_3$, without suitable organic stabiliser, can destabilise the bath. The bleached cotton knit also exhibited oxidative damage in the presence of $Fe^{+3}$ without stabilisers (*Table 5*).

We also studied the combined effect of $Ca^{+2}$ and $Fe^{+3}$ in combined scouring and bleaching for RFD. We found more or less same trend, but noticed that only Saraquest W and Sarastabil M Conc gave the required stabilising action at the prescribed concentration.

This may be attributed to better chelation values for both $Ca^{+2}$ and $Fe^{+3}$. As discussed in our earlier publication *(Selection of Sequestering Agent – More Than Complex? International Dyer – June 2004)*, when both $Ca^{+2}$ and $Fe^{+3}$ are present in the system, $Fe^{+3}$ will be chelated preferentially over $Ca^{+2}$, due to higher stability of $Fe^{+3}$ chelate over $Ca^{+2}$ chelate. Thus, only after chelating $Fe^{+3}$ completely, $Ca^{+2}$ chelation can take place. Both Saraquest W and Sarastabil M Conc have high chelation values for $Fe^{+3}$ and $Ca^{+2}$ and thus showed better performance than other stabilisers. Interestingly, Saraquest 2UD, which has a higher $Fe^{+3}$

chelation value than even Sarastabil M Conc, did not show the required performance, though its $Ca^{+2}$ chelation value is not significantly lower. This could be attributed to the poor chelation constant of active ingredients. Qualitative evaluation of bleached cotton knit samples showed absence of oxidative damage, indicating complete deactivation of $Fe^{+3}$ throughout the bleaching by all stabilisers.

Comparison of Whiteness Index and Yellowness Index was also carried out (*Table 8-11*). There is hardly any difference in Whiteness Index or Yellowness Index of knit samples bleached with $MgCl_2$ or organic stabilisers in soft water or water containing $CaCl_2$. Thus comparison of stabilisers, only on the basis of Whiteness Index or Yellowness Index, does not indicate their performance in actual bleaching. However, the presence of $Fe^{+3}$ in the bleach bath reduces Whiteness Index more than $Ca^{+2}$, and also the increase in Yellowness Index is more than $Ca^{+2}$. Thus, dulling of basic white in cotton knits could be attributed to presence of $Fe^{+3}$ contamination.

Thus, for comparison of various stabilisers, it is advisable to evaluate by their chelation action on $Ca^{+2}$ and $Fe^{+3}$, alone as well as and in combination, as well as residual peroxide at the end of bleaching, action to prevent oxidative damage and finally Whiteness Index and Yellowness Index. Evaluation based on only one parameter could be misleading. Also, $Mg^{+2}$ is not effective in presence of $Ca^{+2}$ and $Fe^{+3}$ in stabilising peroxide. Thus, stabiliser containing $Mg^{+2}$ may not offer any added advantage under these conditions.

$Ca^{+2}$, though, does not lead to oxidative damage and accelerates peroxide decomposition, whereas $Fe^{+3}$ accelerates peroxide decomposition and leads to oxidative damage if not deactivated by suitable chelation. Since it is not possible to carry out bleaching with peroxide in distilled water in industry, it is advisable to use a suitable stabiliser to obtain the required results.

Also, if bleaching is to be carried out for more than 45 min, a dyer must increase the concentration of stabiliser or replace it with a stabiliser having better stabilising action. ❍

**Table 8**

Whiteness Index and Yellowness Index of cotton knits scoured/bleached in distilled water.

| Sr.No. | Products | Whiteness Index | Yellowness Index |
|---|---|---|---|
| 1 | Blank (without stabiliser) | 58.321 | 7.438 |
| 2 | $MgCl_2$ (0.4 g/l) | 62.135 | 6.559 |
| 3 | $MgCl_2$ (2.0 g/l) | 57.337 | 7.772 |
| 4 | Sarastabil MRS (0.3 g/l) | 64.849 | 5.929 |
| 5 | Sarastabil M Conc (0.1 g/l) | 65.858 | 5.630 |
| 6 | Saraquest W (0.1 g/l) | 63.882 | 6.042 |
| 7 | Saraquest W (0.3 g/l) | 63.201 | 6.379 |
| 8 | Saraquest AE (0.15 g/l) | 62.029 | 6.132 |
| 9 | Saraquest 2UD (0.3 g/l) | 63.287 | 6.124 |

**Table 9**

Whiteness Index and Yellowness Index in presence of 80ppm $Ca^{+2}$ :-

| Sr.No. | Products | Whiteness Index | Yellowness Index |
|---|---|---|---|
| 1 | Blank (without stabiliser) | 59.958 | 7.019 |
| 2 | $MgCl_2$ (0.4 g/l) | 62.404 | 6.553 |
| 3 | Sarastabil MRS (0.3 g/l) | 64.185 | 6.107 |
| 4 | Sarastabil M Conc (0.1 g/l) | 61.766 | 6.545 |
| 5 | Saraquest W (0.1 g/l) | 63.398 | 6.258 |
| 6 | Saraquest AE (0.15 g/l) | 63.668 | 6.327 |
| 7 | Saraquest 2UD (0.3 g/l) | 60.608 | 7.050 |

**Table 10**

Whiteness Index and Yellowness Index in presence of 3ppm $Fe^{+3}$

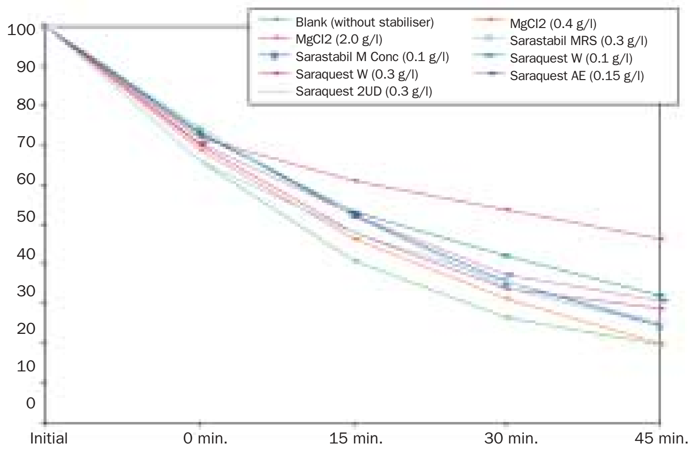
| Sr.No. | Products | Whiteness Index | Yellowness Index |
|---|---|---|---|
| 1 | Blank (without stabiliser) | 56.579 | 10.396 |
| 2 | $MgCl_2$ (0.4 g/l) | 56.634 | 10.326 |
| 3 | Sarastabil MRS (0.3 g/l) | 57.275 | 10.338 |
| 4 | Sarastabil M Conc (0.1 g/l) | 58.961 | 9.842 |
| 5 | Saraquest W (0.1 g/l) | 57.585 | 10.353 |
| 6 | Saraquest AE (0.15 g/l) | 56.940 | 10.486 |
| 7 | Saraquest 2UD (0.3 g/l) | 57.585 | 10.190 |

**Table 11**

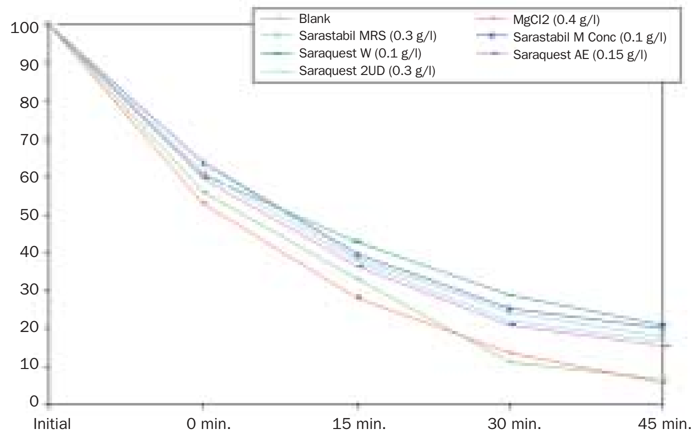
Whiteness Index and Yellowness in presence of 80ppm $Ca^{+2}$ + 3ppm $Fe^{+3}$

| Sr.No. | Products | Results Whiteness Index | Yellowness Index |
|---|---|---|---|
| 1 | Blank (without stabiliser) | 56.916 | 11.898 |
| 2 | $MgCl_2$ (0.4 g/l) | 56.336 | 10.564 |
| 3 | Sarastabil MRS (0.3 g/l) | 56.262 | 10.749 |
| 4 | Sarastabil M Conc (0.1 g/l) | 56.952 | 10.671 |
| 5 | Saraquest W (0.1 g/l) | 56.946 | 10.948 |
| 6 | Saraquest AE (0.15 g/l) | 56.336 | 11.385 |
| 7 | Saraquest 2UD (0.3 g/l) | 56.000 | 11.198 |

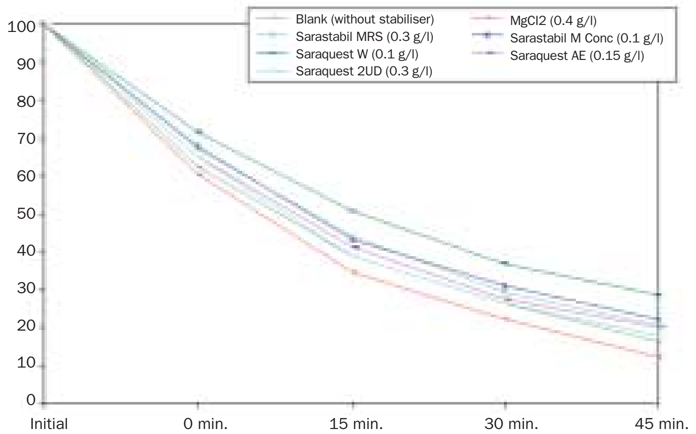
## Fig.1 Kinetics of bleaching in distilled water



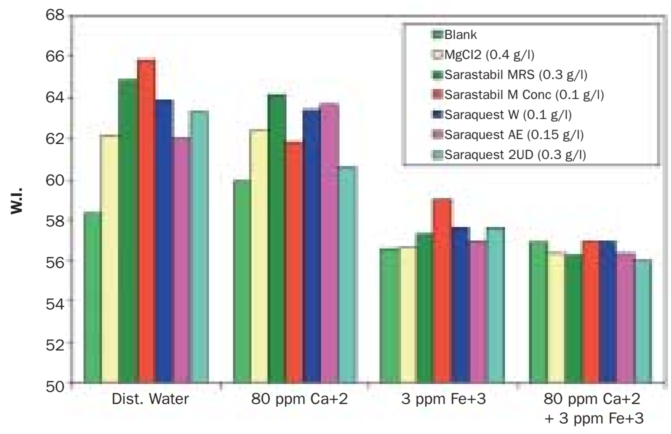

## Fig.4 Kinetics of bleaching in presence of 80 ppm $Ca^{+2}$ + 3 ppm $Fe^{+3}$



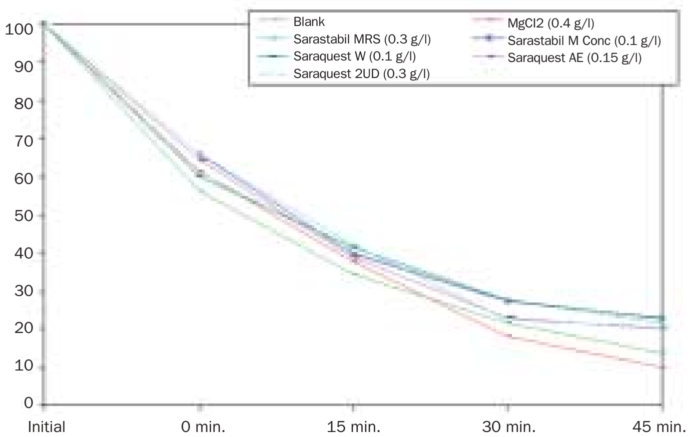

## Fig.2 Kinetics of bleaching in presence of 80 ppm $Ca^{+2}$




## Fig.5 Whiteness Index




## Fig.3 Kinetics of bleaching in presence of 3 ppm $Fe^{+3}$




## Fig.6 Yellowness Index