

# Sustainable low liquor ratio dyeing of wool with acid dyes: Effect of auxiliaries on agglomeration of dye molecules in a dyebath and dyeing uniformity

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## ABSTRACT

The use of a low-liquor ratio (1:10 or less) in the dyeing of wool has several economic and environmental benefits, such as lower energy usage and smaller quantity of auxiliaries are required compared to the traditional dyeing method. However, the reduction in liquor ratio increases the occurrence of agglomeration of dyes causing uneven dyeing. The aim of this study is to develop a low-liquor dyeing method for wool with acid dyes that could potentially be applied to larger scale industrial practices. In this work, the feasibility of application of several chemical auxiliaries to prevent the agglomeration of dyes in dyebaths and also for improving the dyeing uniformity in the low liquor ratio dyeing of wool fabric with three acid dyes, has been investigated. Optical microscopy was used to evaluate the performance of various auxiliaries to prevent the agglomeration of dyes in a dyebath. The dyeing uniformity was assessed by measuring the colour difference in various parts of the same dyed fabric by a

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hand-held reflectance spectrophotometer. It was found that Teric G12A6 showed the best results in terms of prevention from the agglomeration of dyes and the dyeing uniformity produced for all three acid dyes investigated. The low liquor ratio dyeing of wool fabrics with acid dyes using Teric G12A6 as a dye agglomeration preventer is equally efficient as the traditional high liquor ratio dyeing in terms of colour strength and uniformity in dyeing. The developed method could reduce dyeing cost and environmental footprint compared to the traditional dyeing of wool.

*Keywords:* low liquor ratio dyeing; sustainable dyeing; energy savings; dye agglomeration; colour difference; acid dyes

## **1. Introduction**

Dyeing of textiles is an energy-intensive process as it requires boiling textiles in a large quantity of dye liquor (30 to 40 times of total weight of textile materials) containing a cocktail of electrolyte, wetting agent, dye levelling agent and pH buffering agent for 30 to 120 minutes (depending on the depth of shade). The consumption of these auxiliary chemicals depends on the liquor ratio of dyeing. The 'liquor ratio' of a dye bath is the ratio of substrate material to the dye liquor. Energy consumption in dyeing can be minimised either by reducing the liquor ratio of dyeing or by reducing the dyeing temperature. Both of them have merits and demerits. Low liquor ratio dyeing causes aggregation of dye molecules in the dyebath causing uneven dyeing. Conversely, the colour fastness to washing and rubbing is compromised for the fabrics dyed by low-temperature dyeing methods as dye molecules are not fully diffused into the fibres causing ring dyeing [Welham, 2013]. Energy savings also can be realised by modifying dyeing machinery making them more energy efficient than

conventional dyeing machinery or by changing dyeing techniques. For example, dyeing machinery can be made energy efficient by reducing their water usage through machinery modifications, such as airflow dyeing machine where dye liquor is atomised, mixed with high pressure airflow and then is sprayed on the fabric, which considerably reduces water usage [Siu et al., 2016]. Nylon fibre can be dyed at room temperature on the melt spinning machine by using the solvent crazing technique [Kale et al., 2015] that considerably reduces energy demand for dyeing.

To enable low temperature dyeing of textile fibre, it is necessary to increase the affinity of the dye to the fibre by chemical modifications of the fibre [Kantouch et al., 2005] or by using a dye carrier for the dyeing of polyester with disperse dyes [Pasquet et al., 2013]. It was found that the pre-treatment of wool fibre with a lipase enzyme enhanced wool fibre's ability to absorb reactive dyes [Kantouch et al., 2005]. The treatment of wool fibre with a bacterial protease enzyme enhanced the absorption of acid dyes by wool fibre from 77% for the untreated to 90% for the enzyme-treated wool fibre [Periolatto et al., 2010]. It was reported that the modification of silk fibre by atmospheric plasma in the presence of nitrogen/helium gases enabled dyeing of silk fibre at 40°C [Teli et al., 2015] instead of at boil. On the other hand, Wang et al., utilised a quite different approach as they added sodium-5-sulfo-bis(hydroxyethyl)-isophthalate and 2-methyl-1,3-propanediol to the spinning dope of polyester, which enabled dyeing of that polyester at boil under atmospheric pressure [Wang et al., 2016]; otherwise polyester fibres are usually dyed at 130 °C under high pressure. Low liquor ratio dyeing [Xie et al., 2011] and low liquor ratio micelle dyeing [Liu et al., 2013] also have been investigated to reduce the energy consumption in dyeing of textiles. These methods only provide limited success as the level of reduction in dyeing cost achieved is only marginal compared to the conventional methods. Machinery modification provides energy savings to a certain level. The fibre modification techniques may even increase the processing

cost as an extra step is needed for the modification of fibre and therefore energy saving achieved could be meaningless. The low liquor ratio dyeing could be an option to make wool dyeing energy efficient. There are several advantages associated with minimising the liquor ratio of a dye bath. By minimising the liquor ratio, the volume of dye liquor is reduced and hence the heating expenses are reduced, making the process more economical compared to traditional dyeing methods. Other economic advantages include reduced water and chemical auxiliary usage. These advantages whilst benefitting the industry by reducing the costs of the wool dyeing process, simultaneously benefit the environment. The use of a low liquor ratio during dyeing will reduce the volume of effluent to treat. Furthermore, there is a scarcity of water in many places in the world, and thus it is desirable to reduce water usage in dyeing. Therefore current research is emphasised on the reduction of the liquor ratio in dyeing to sustain the dyeing process [Shamey and Zhao, 2014].

However, as the liquor ratio is decreased, correspondingly the concentration of dye molecules in the dye bath increases. Agglomeration of dye molecules in a dyebath not only causes uneven dyeing but also reduces migration of dyes from the dyebath to the interior of fibre, which not only increases the loss of dyes in effluent but also increases the load on the effluent treatment plant. When electrolytes (commonly sodium chloride or sulphate) are added to a concentrated dye solution, self-association of dye molecules takes place, forming large dye particles that are suspended in dye liquor. This self-association of dyes is called 'dye agglomeration'. Dye agglomeration is a mass conserving but number reducing process that shifts the particle distribution towards larger sizes, which affects the transport of particles as larger particles tend to settle more rapidly under gravity but diffuse more slowly.

Agglomeration also reduces available particle surface area for chemical reaction. There are several models, such as Brownian agglomeration, gravitational agglomeration, turbulent agglomeration and electrostatic agglomeration used to describe agglomeration of particles. Of

them, Brownian agglomeration is the most popular model. Brownian motion is the random motion of particles suspended in a liquid resulting from their collision with atoms or molecules. Shahub and Williams carried out an investigation where they studied the effect of van der Waals, viscous and electrostatic forces on the collision efficiency for the Brownian coagulation of particles [Shahub and Williams, 1988]. They used the Boltzmann charge distribution on the particles. They found that for highly charged particles, the electrostatic effect dominates, whilst for particles with up to approximately 10 unit charges, the van der Waals, viscous and electrostatic forces interact in a complex fashion which significantly alters the conventional rate of coagulation predicted by classical theory. In a dye solution dyes are dispersed at the molecular level but when they agglomerate, they form particles and therefore their agglomeration can be described by agglomeration by Brownian motion. Dye agglomeration occurs when the self-association of dye molecules in the solution due to electrostatic attractions and hydrophobic interactions becomes energetically favourable [Zollinger, 2003]. It is more severe in the case of dyeing to deep shades than to light shades because of the high concentration of dyes used for deeper shades. It was also found that agglomeration of dyes could affect the equilibrium of dye-fibre concentration as large dye particles cannot enter into fibre [Taylor, 2000]. Reducing this dye agglomeration is the key to enabling the commercial application of low liquor ratio dyeing as an eco-friendly alternative to current practices.

There is very few literature currently published on the topic of low liquor ratio dyeing and the reduction of dye agglomeration. Previous studies reported the application of ultrasound for improving dispersion of dye molecules in a dyebath and also for enhancing migration of dyes from dyebath to fibre for the dyeing of acrylic [Kamel et al., 2010], cotton [Tissera et al, 2016], wool [Ferrero and Periolatto, 2012] and other fibres [Vajnhandl et al., 2005] with basic, acid and reactive dyes. Ultrasound has also been investigated for the deagglomeration

of an acid dye molecules in the low liquor ratio dyeing of wool fibre [Hassan and Bhagvandas, 2016]. The use of ultrasound adds cost (energy) and also a necessary change in dyeing equipment. It was reported that the agglomeration behaviour of direct dyes was a complicated function that was affected by several parameters including temperature, electrolyte, surfactant type and dye concentration [Ferus-Comelo and Greaves, 2002]. Their study concluded that while dye agglomeration was reduced by an increase in temperature, a portion of dye molecules still remained agglomerated up to 90 °C. Non-ionic surfactants can also be used to reduce dye agglomeration by the formation of stable micelles between the dye and the surfactant [Lewis, 1992]. Low liquor ratio dyeing has also been investigated by micelle dyeing by forming dye-surfactant micelles using dibutyl maleic acid ester sodium sulphate surfactant for dyeing cotton with reactive dyes (Xie et al., 2011). Blus and Bemska also found that the addition of non-ionic surfactants can break down dye agglomerates by forming a surfactant-dye complex [Blus and Bemska, 2010]. However, none of these studies dealt with a low liquor ratio dyeing using a chemical auxiliary; thus making this topic of study relatively unexplored.

In a dispersion of agglomerated dye particles, the dispersion is usually polydisperse, composed of particles of various sizes. Agglomeration occurs when dye particles collide and adhere. When they agglomerate, they adhere strongly and the resulting agglomerates cannot be redispersed. Within a given disperse medium, the dispersed particles undergo attractive van der Waals forces as well as repulsive electrostatic interactions operating between electric double layers on neighbouring particles and also solvation effects at low distances of particle separation and Brownian motion. If the attractive forces dominate, then the particles coalesce and agglomerate but if the repulsive forces dominate, then a stable system is formed. Therefore appropriate auxiliaries are added to the dispersion to increase the repulsive forces.

Water-soluble dyes are usually blended with anionic surfactants to reduce agglomeration [Reife and Freeman, 1996].

In this study, the suitability of several chemical auxiliaries to assist in the low liquor ratio dyeing of wool, to prevent agglomeration of dye molecules in a dyebath and also to improve the dyeing uniformity in the dyeing of wool fabrics, have been investigated. The dyeing treatment was replicative of commercial dyeing industry processes. The ability of the chemical auxiliaries to improve the overall dyebath exhaustion was investigated by a visible reflectance spectrophotometry. The most popular dye type for dyeing wool fibre is acid dyes and therefore low liquor ratio dyeing was investigated using this particular class of dyes.

## **2. Experimental**

### *2.1. Materials*

The substrate used was a 210 g/m<sup>2</sup> 2/2 twill woven fabric having 34 ends/cm and 24 picks/cm. Three commercially available acid dyes, Sandolan Red MF-2BL (C.I Acid Red 336), Sandolan Blue MF-BLN (C.I. Acid Blue 350) and Sandolan Golden Yellow MF-RL (C.I. Acid Orange 67), were chosen. All the dyes were purchased from Clariant Chemicals (Switzerland). The auxiliaries investigated to prevent dye agglomeration were Linsegal WRD (modified ethylene oxide condensation products), sodium dodecyl benzene sulphonate (DBS), Span 80, Teric G13A9 (isotridecanol-based ethyl ethoxylate), dodecyl benzene sulphonic acid, and Teric G12A6 (C12-C15-based alcohol ethoxylate). Linsegal WRD was purchased from Chemie Impex (Germany), and Teric G12A6 and Teric G13A9 were purchased from Huntsman Chemicals (USA). Teric GN9 (a non-ionic surfactant) and Sandozin MRN (a wetting agent) were purchased from Huntsman Chemicals (USA) and

Clariant Chemicals (Switzerland) respectively. Acetic acid and all other chemicals were purchased from Sigma-Aldrich Limited (USA).

## *2.2. Dyeing wool with acid dyes*

Prior to dyeing, wool fabric samples were scoured in a 9-L capacity Vald Henriksen dyeing machine using 2 g/L Teric GN9 and 0.25 g/L Sandozin MRN (Clariant, Switzerland) at 50 °C for 20 min. After scouring, the material was rinsed with hot tap water at 60 °C and again in cold water to remove the residual surfactant.

All dyeings were carried out in an Ahiba laboratory dyeing machine using a 1:10 materials to water ratio. The bath was dosed with 10% on the weight of fibre (owf) sodium sulphate, 0.25 g/L Sandozin MRN and the required quantity of a dye-agglomeration preventing auxiliary. The applied dosage of all the agglomeration preventing agents investigated in this work was 2 g/L. The temperature of the bath was set at 30 °C, the wool fabric sample was introduced, and was run for 10 min. The required quantity of dye (5% owf) was added to the dyebath and the pH was adjusted to 4.5 with acetic acid and sodium acetate solutions. The machine was run for another 10 min and the temperature was then raised to 98 °C at 2 °C/min and held for 60 min, after which the dyebath was cooled to 45 °C at 2 °C/min and the dye liquor was drained. The samples were then dried in an oven at 65 °C. The dyeing of the ‘Control (1:30)’ and the ‘Control (1:10)’ wool fabrics was carried out under the same conditions but using a liquor ratio 1:30 and 1:10 respectively and also without using any dye agglomeration preventer.

## *2.3. Assessment of dye agglomeration*



After addition of all auxiliaries and at 30 °C, a small quantity of dye solution (3 drops) from the dyebath was placed on a microscope glass slide and the size of dye particles were observed using a Karl Zeiss optical microscope. A lack of visible of dye microparticles under the microscope was treated as no agglomeration of dye molecules.

#### *2.4. Colour measurement*

The colour measurements of various dyed samples were carried out according to a published literature (Hassan and Hawkyard, 2002). The reflectance values and K/S values (at the appropriate wavelength of maximum absorption for each dyeing) of the dyed samples were measured using a Datacolor Spectraflash 600 spectrophotometer interfaced to a personal computer. Samples were measured under illuminant D65, using a 10° standard observer with UV component and specular excluded. Each of the samples was folded three times to realise a total of eight layers of fabric. A total of four measurements were made on each sample and the average value is reported here. The colour difference was spectrophotometrically measured by measuring CIE L\*, a\*, b\* colour difference ( $\Delta E$ ) between the lighter and darker parts of the same dyed sample under illuminant D65, using a 10° standard observer by a Mahlo Spectro-Guide 45/0 gloss Color Spectrophotometer (Mahlo GmbH, Germany). The dyeing uniformity was assessed by measuring the colour difference in various parts of the dyed fabric. The lower the colour difference the higher the uniformity in dyeing.

### **3. Results and discussion**

The decrease in liquor ratio in the dyebath favours agglomeration of dyes as the dye solution becomes concentrated and dye molecules come near to each other compared to dye molecules in a diluted solution. Agglomeration of dyes produces uneven dyeing and also reduces migration of dye molecules from the dyebath to the interior of the fibre resulting in the formation of lighter shades than usual.

Fig. 1 shows the effect of reduction in liquor ratio from 1:30 to 1:10 with no agglomeration preventing auxiliaries present. It is evident that at the higher liquor ratio almost no agglomeration occurs which is evident in Fig. 1 as both Sandolan Red MF-2BL and Sandolan Blue MF-BLN dyes produced no agglomeration when the materials to liquor ratio was 1:30. However, when the liquor ratio was dropped to 1:10, both dyes agglomerated forming large dye particles. Sandolan Red MF-2BLN formed agglomerated dye particles as big as 100  $\mu\text{m}$  but in the case of Sandolan Blue MF-BLN, the highest size of agglomerated dye particles was 50  $\mu\text{m}$ .

### *3.1. Effect of various auxiliaries on agglomeration of dyes*

De-agglomeration behaviour of dye molecules by the addition of various auxiliaries was evaluated by observing the agglomerated dye particle size by an optical microscope. Fig. 2 shows optical microscopic images of Sandolan Blue MF-BLN dye particles after the addition of various dye agglomeration preventing agents at 1:10 liquor ratio. It was found that in the presence of sodium sulphate, Sandolan Blue MF-BLN dyebath produced polydisperse dye particles through agglomeration of dye molecules. The size of dispersed dye particles was as big as 50  $\mu\text{m}$ . The addition of Span 80 to the sodium sulphate containing dyebath hardly changed the size of the agglomerated dye particles. The addition of Teric 13A9 reduced the size of the agglomerated dye particles to almost half. The auxiliary that showed the best

prevention from the agglomeration of dye molecules was Teric G12A6 as the size of dye particles were the lowest of the auxiliaries investigated and most of the dye molecules were in solution and invisible when viewed under a microscope. The second best de-agglomerating agent for Sandolan Blue MF-BLN was Linsegal WRD as only a few dye particles were a couple of microns in size and it is expected that they would be disintegrated with the progress in dyeing at boiling temperatures. DBS and Teric 13A9 also showed some levels of performance as de-agglomerating agent but they were not as good as Teric G12A6, which showed the best performance in terms of de-agglomeration of acid dyes at low liquor ratio (1:10).

Fig. 3 shows optical microscopic images of Sandolan Red MF-2BL dye particles after the addition of various dye agglomeration preventing agents at 1:10 liquor ratio. The control dye solution produced agglomerated particles as big as 100  $\mu\text{m}$ . With the addition of Span 80 to dye bath, instead of forming particles, dye molecules formed a network and some links of the network were as thick as 20  $\mu\text{m}$ . In the case of addition of Linsegal WRD, the thickness of links was up to 50  $\mu\text{m}$  but the formed network was not dense. The addition of DBS formed an agglomeration of various small sized particles. Teric G12A6 was found to be the best de-agglomerating agent for Sandolan Red MF-2BL and the second best one was Teric 13A9. In the case of Sandolan Golden Yellow MF-RL, again Teric G12A6 provided the best performance as a dye agglomeration preventing agent. In the case of Sandolan Red MF-2BL dye, the addition of some auxiliaries formed network structures of dye molecules, but for the other two dyes, no such kind of network structure was observed. In summary, Teric G12A6 was found to be the best auxiliary that provided the best protection against agglomeration of dyes at 1:10 liquor ratio for all three dyes investigated in this work.

### *3.2. Effect on colour strength*

The wavelength of maximum absorption for three dyes, Sandolan Blue MF-BLN, Sandolan Golden Yellow MF-RL and Sandolan Red MF-2BL were at 620, 460 and 520 nm, respectively and the colour strength was measured at these wavelengths for the fabric dyed with the respective dyes. The higher liquor ratio (1:30) dyeing of wool using sodium sulphate as an electrolyte was used as a benchmark of uniformity in dyeing and colour intensity that would ideally be replicated by the low liquor dyeing process.

Fig. 5 shows the average colour strength of wool fabrics dyed with the three acid dyes using a range of auxiliaries to reduce dye agglomeration in a dyebath. The colour strength values determine the depth of the shade, i.e. the higher the colour strength, the deeper the shade. The colour strength of wool fabric samples dyed at liquor ratio 1:30 without using any agglomeration preventing agent produced colour strength 26.63, 29.50 and 27.74 for the Sandolan Blue MF-BLN, Sandolan Red MF-2BL and Sandolan Golden Yellow MF-RL dyes, respectively. However, when the liquor ratio was decreased, the colour strength decreased to 25.17, 28.15 and 26.17 (colour measurements were taken at the deepest coloured areas) respectively for the same dyes for the same applied doses of dyes. However, the dyeing using 1:30 liquor ratio produced very uniform dyeing but the liquor ratio 1:10 produced very uneven dyeing. It indicates that the reduction in liquor ratio affected the absorption of dyes into the fabric due to the agglomeration of dye molecules in the dyebath. It is evident that most of the auxiliaries investigated in this work marginally increased the colour strength of the dyed samples as the measurement of colour strength was carried out at the darkest part of a dyed fabric. It was observed that in the case of control dyeing using liquor ratio 1:10 and also in the case of low liquor ratio dyeing using Span 80 and Teric 13A9, a portion of dye remained in the bath after the dyeing process indicating poor dye uptake. The highest improvement in colour strength was shown by DBS for all three dyes. Teric G12A6 also

showed improvement in colour strength for Sandolan Red MF-2BL, similar to the improvement in colour strength observed by using DBS. The lowest improvement in colour strength was observed for Span 80 for all three dyes investigated.

At low liquor ratios, agglomeration of dyes occurs that reduces migration of dyes from the dyebath to the interior of the fibre. As the dye particle size becomes bigger due to agglomeration, they cannot penetrate into the fibre. Comparatively larger dye particles may block the pores of the fibres and therefore further dye molecules cannot go into the interior of the fibre resulting in poor migration of the dyes resulting in decreased colour strength. Therefore we can conclude that the low liquor ratio dyeing without using dye agglomeration preventers is equally efficient as the high liquor ratio dyeing but the uniformity in dyeing is adversely affected. The use of Teric G12A6 in the low liquor ratio dyeing is equally efficient as the high liquor ratio dyeing in terms of colour strength and the uniformity in dyeing.

### *3.3. Effect on CIE L\*,a\*,b\* values*

Table 1 shows CIE L\*a\*b\* and h° values of wool fabrics dyed with Sandolan Red MF-2BLS, Sandolan Blue MF-BLN and Sandolan Golden Yellow MF-RL dyes in the presence of various dye agglomeration preventing agents. The lightness (L\*) is inversely related to the depth of the shade, i.e. the higher the lightness value the lower the depth of shade. It is evident that in the case of control dyeing (without dye agglomeration preventers) the L\* values of dyed fabrics increased when the liquor ratio decreased from 1:30 to 1:10, indicating the reduction in depth of shade caused by agglomeration of dyes, which prevented migration of dyes from the dyebath to the fibre resulting in decreased depth of shade. The L\* values for the wool fabrics dyed with Sandolan Red MF-2BLS, Sandolan Blue MF-BLN and Sandolan Golden Yellow MF-RL using liquor ratio 1:30 were 33.73, 23.62 and 52.98, respectively.

However, when the liquor ratio was decreased, the corresponding L\* values increased to 37.08, 26.91 and 58.65 respectively. Of the dye agglomeration preventers investigated, only the wool fabric samples dyed in the presence of Teric G12A6 achieved the L\* values near to the L\* values of the wool fabric dyed with all three dyes by control dyeing using the liquor ratio 1:30. DBS in the case of Sandolan Red MF-2BLS dye and Linsegal WRD in the case of Sandolan Blue MF-BLN produced marginally dipper shades compared to the shade produced by the control fabric dyed with these dyes but the uniformity in dyeing was very poor for them compared to the very uniform dyeing produced by the control fabric at 1:30 liquor ratio. These results suggest that Teric G12A6 is the best dye agglomeration preventer.

#### *3.4. Effect on colour difference ( $\Delta E$ ) and uniformity in dyeing*

Usually, colour difference lower than 1 is acceptable, as the human eye can hardly perceive a colour difference of less than 1. Fig. 6 shows the colour difference of wool fabric using control dyeing at liquor ratios 1:30 and 1:10 and also wool fabrics dyed at liquor ratio 1:10 in the presence of various auxiliaries to reduce dye agglomeration. It can be seen that all three dyes produced very uniform shades in wool fabric samples when dyed at liquor ratio 1:30 as the colour difference values in various parts of the dyed samples for wool fabric dyed with Sandolan Blue MF-BLN, Sandolan Red MF-2BL and Sandolan Golden Yellow MF-RL without using any agglomeration preventing agent were 0.57, 1.0 and 0.36 respectively. On the other hand, when the liquor ratio was decreased to 1:10, the dyeing uniformity was adversely affected, increasing the colour difference values to 8.56, 5.25 and 9.9 for Sandolan Blue MF-BLN, Sandolan Red MF-2BL and Sandolan Golden Yellow MF-RL respectively. Fig. 7 shows optical images of actually dyed samples. Of the auxiliaries investigated, Teric G12A6 produced the most uniform dyeing for all three acid dyes (produced the lowest colour

difference) and was close to that achieved using the higher liquor ratio (1:30). On the other hand, in the cases of Span 80, DBS, and Linsepal WRD, the dyeing uniformity was the poorest for all three acid dyes (Fig.7). However, the dyeing uniformity produced by the all the auxiliaries was far better than the uniformity in dyeing produced without them.

Although dyeing of acid dyes using DBS showed the highest colour strength, it also produced the least dyeing uniformity. Teric G12A6 was overall the best performer in terms of dyeing levelness and the colour strength produced. Teric G12A6 is a C12-C15-based alcohol ethoxylate that probably increased dissolution of dyes in the dyebath and also electrostatically prevented agglomeration of dye molecules and therefore increased levelness of dyeing. As Teric G12A6 showed the best results, it would be the best for further optimisation.

### *3.5. Effect of concentration of Teric G12A6*

Table 2 shows the effect of an increase in Teric G12A6 concentration on the colour difference and also the uniformity in dyeing. It can be seen that the colour difference and uniformity in dyeing increased with an increase in Teric G12A6 concentration for all three dyes investigated and at 3 g/L produced the best uniform dyeing as the colour difference reduced to 0.5, 0.10 and 0.69 at that level of application for the fabric dyed with Sandolan Red MF-2BLS, Sandolan Blue MF-BLN and Sandolan Golden Yellow MF-RL, respectively. Therefore we can conclude that 3 g/L dosage is the optimum dosage to prevent agglomeration of dyes and also to achieve the uniformity in dyeing without affecting the depth of shade.

## **4. Conclusions**

In this work, we demonstrated that acceptable low liquor ratio dyeing of wool fibres with

acid dyes is possible by using appropriate auxiliaries. Reduction in liquor ratio to 1:10 produces uneven dyeing because of agglomeration of dye molecules, but the application of particular textile auxiliaries can reduce agglomeration, improve colour intensity and also produce more even dyeing by increasing the solubility of dyes in a dyebath conditions. The chemical auxiliary identified as the most suitable for the prevention of agglomeration of dye molecules during low-liquor (1:10) ratio dyeing of wool textile is Teric G12A6, which produced very even shades for all three dyes investigated. Although the addition of DBS helped in increasing migration of dyes from dyebath to fibre, it produced uneven dyeing and was not effective for deagglomeration. The use of these chemical auxiliaries under conditions that would be used in industry and the results that have been achieved potentially enables the application of low liquor dyeing in the wool textile dyeing industry. The developed process can be used to improve the environmental performance of wool dyeing.

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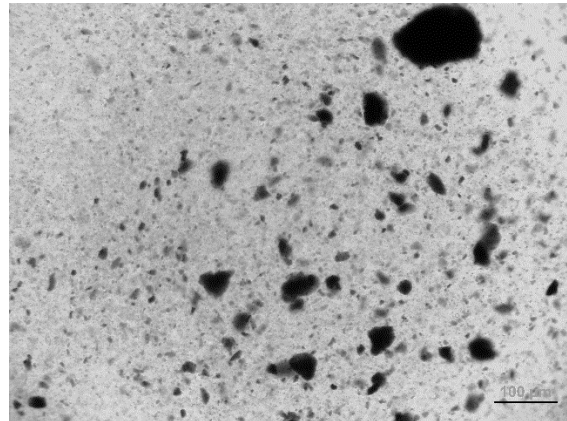
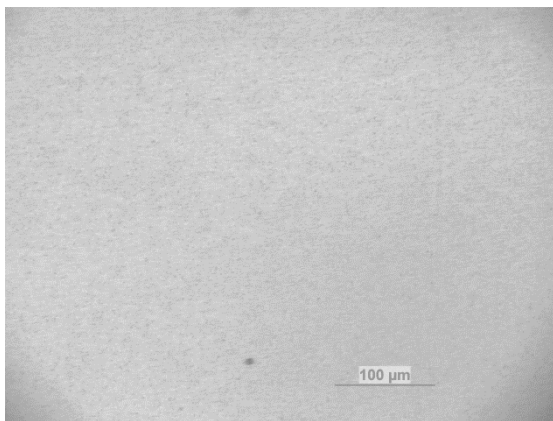
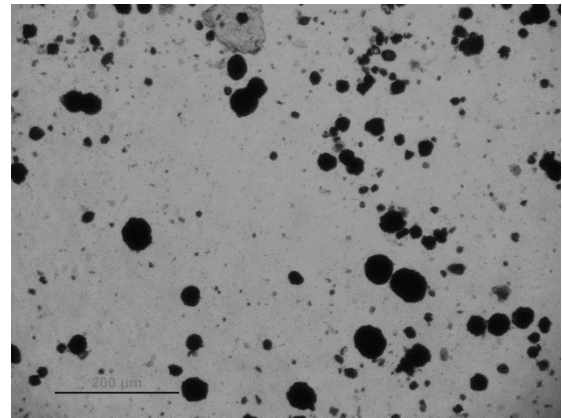
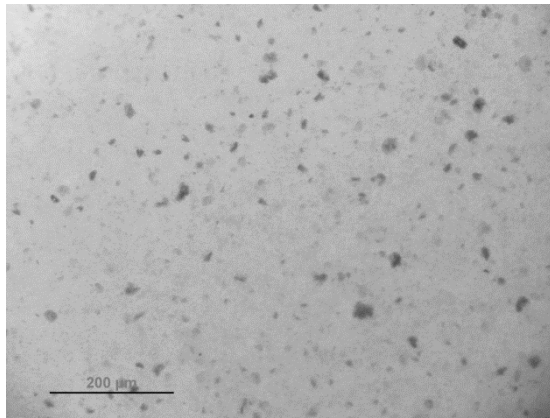
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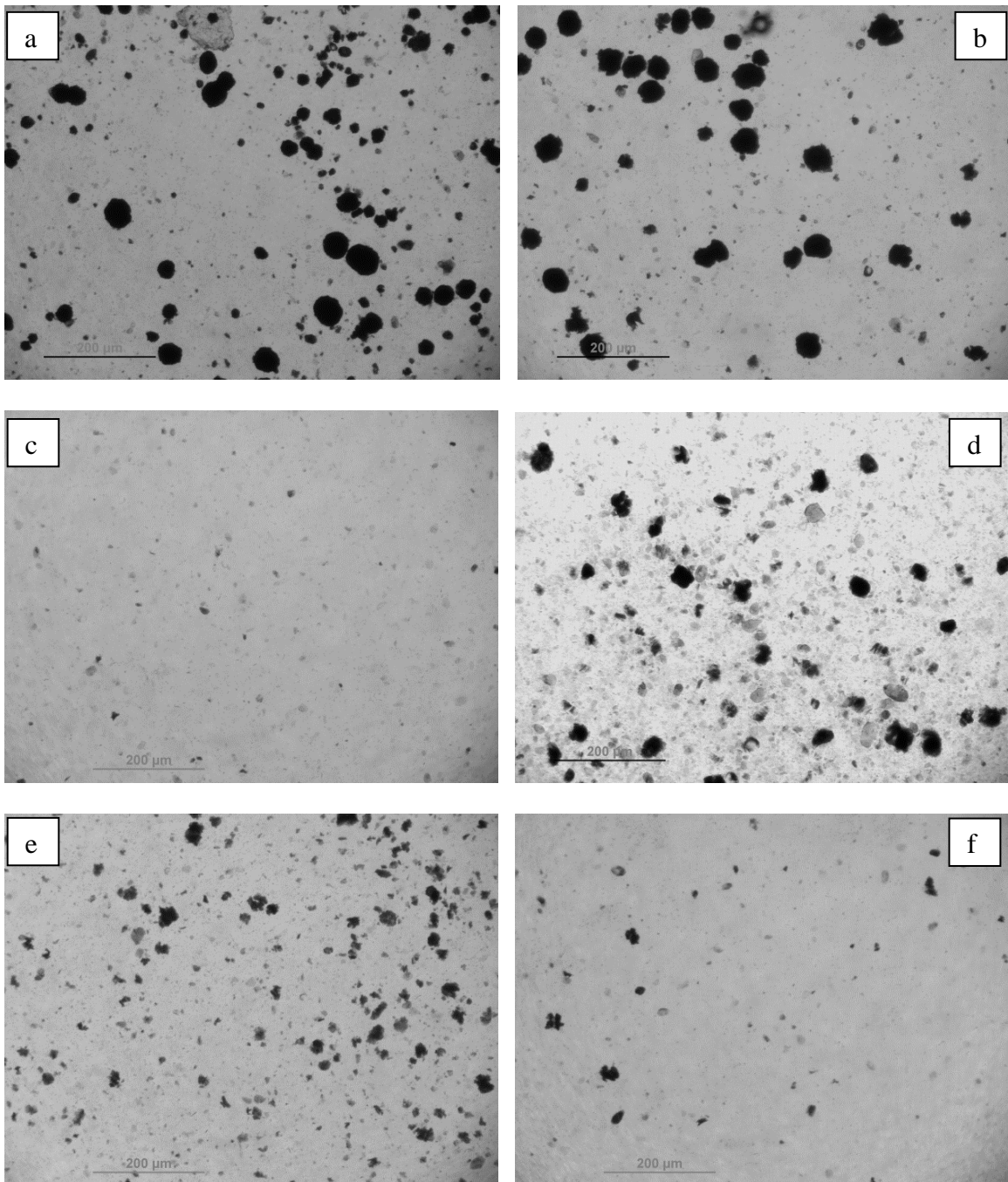
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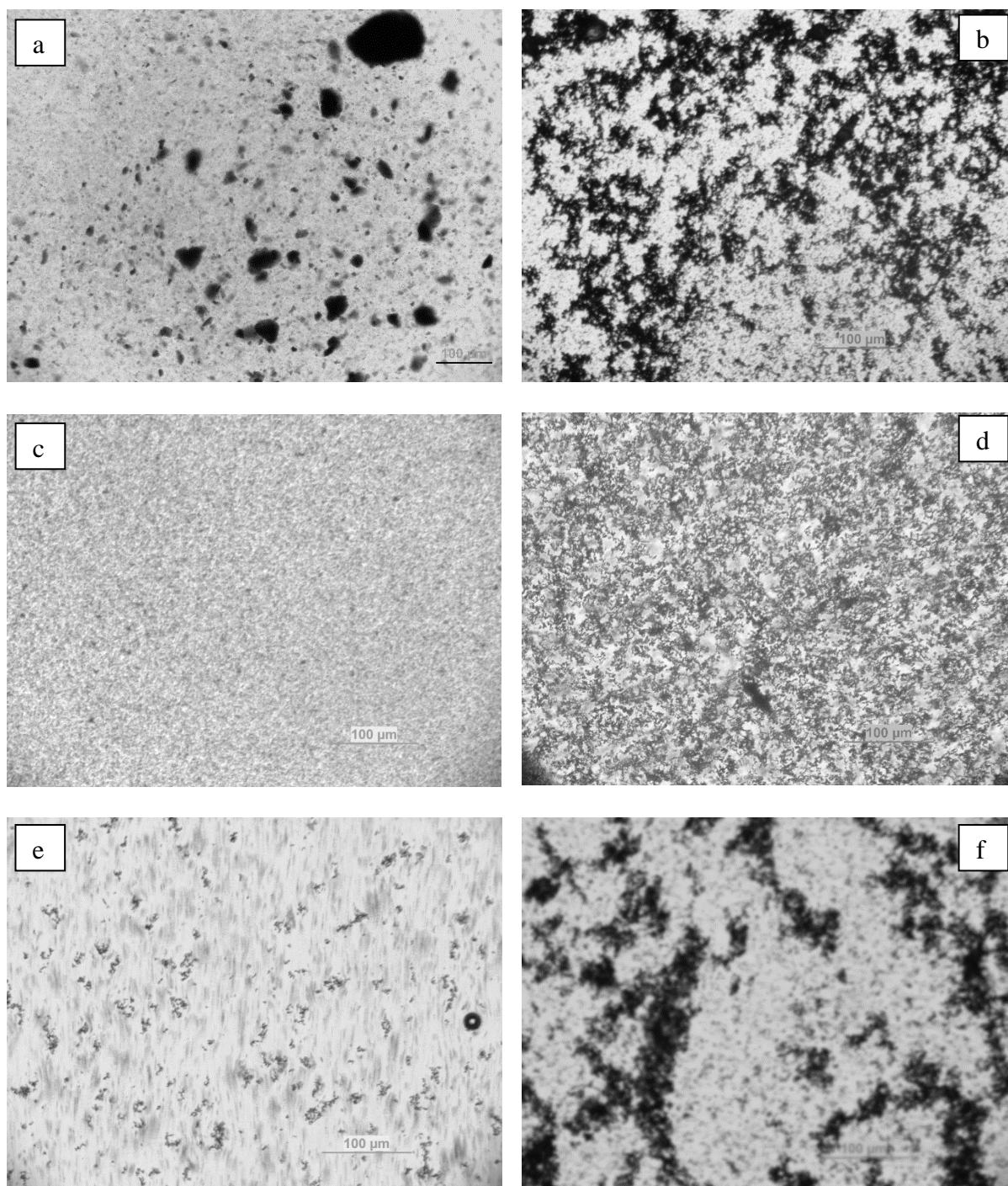
Liquor ratio 1:30

Liquor ratio 1:10

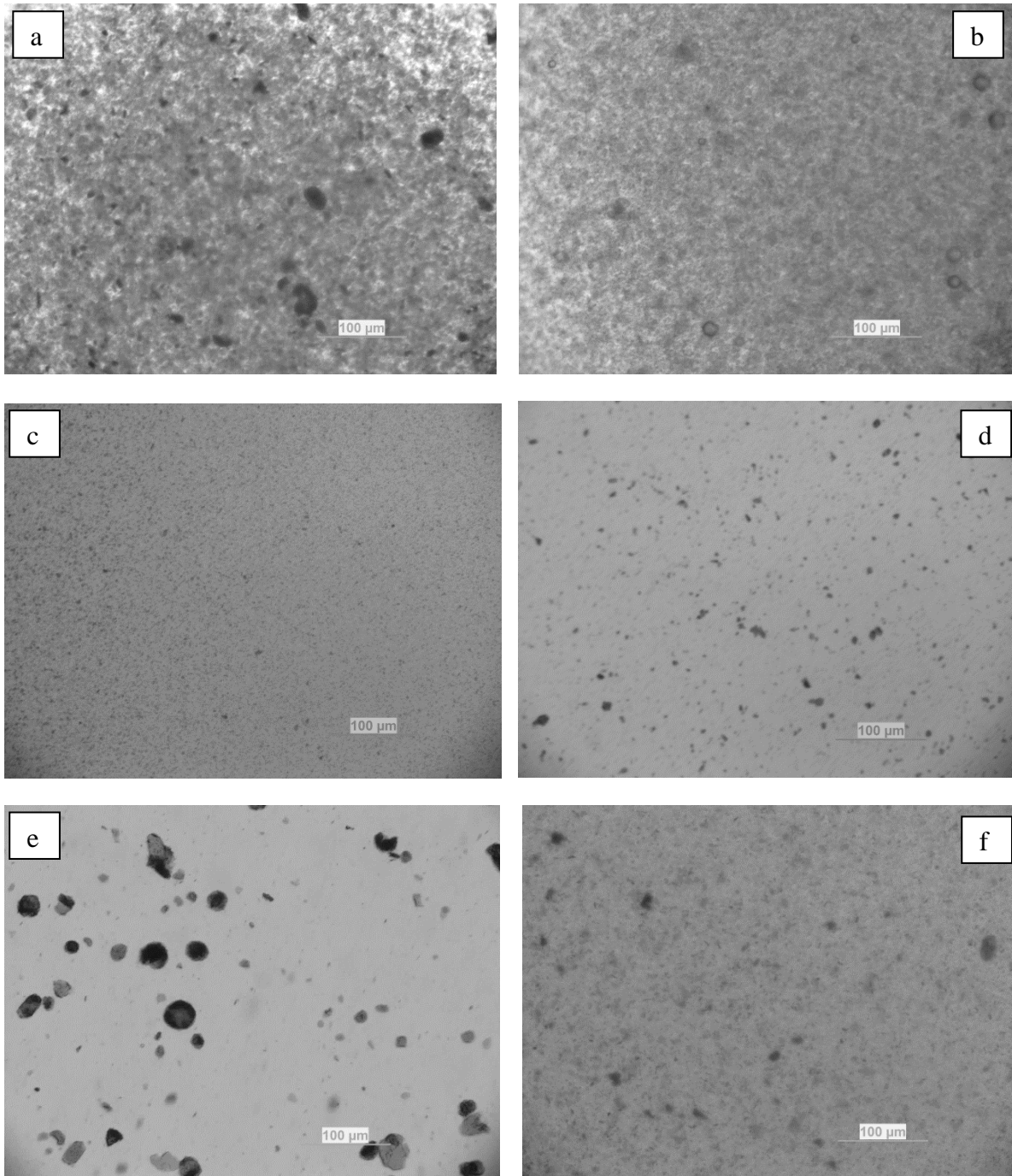
**Fig. 1.** Effect of decrease in liquor ratio on the size of dye agglomeration for Sandolan Blue MF-BLN (top) and Sandolan Red MF-2BL (bottom) acid dyes.



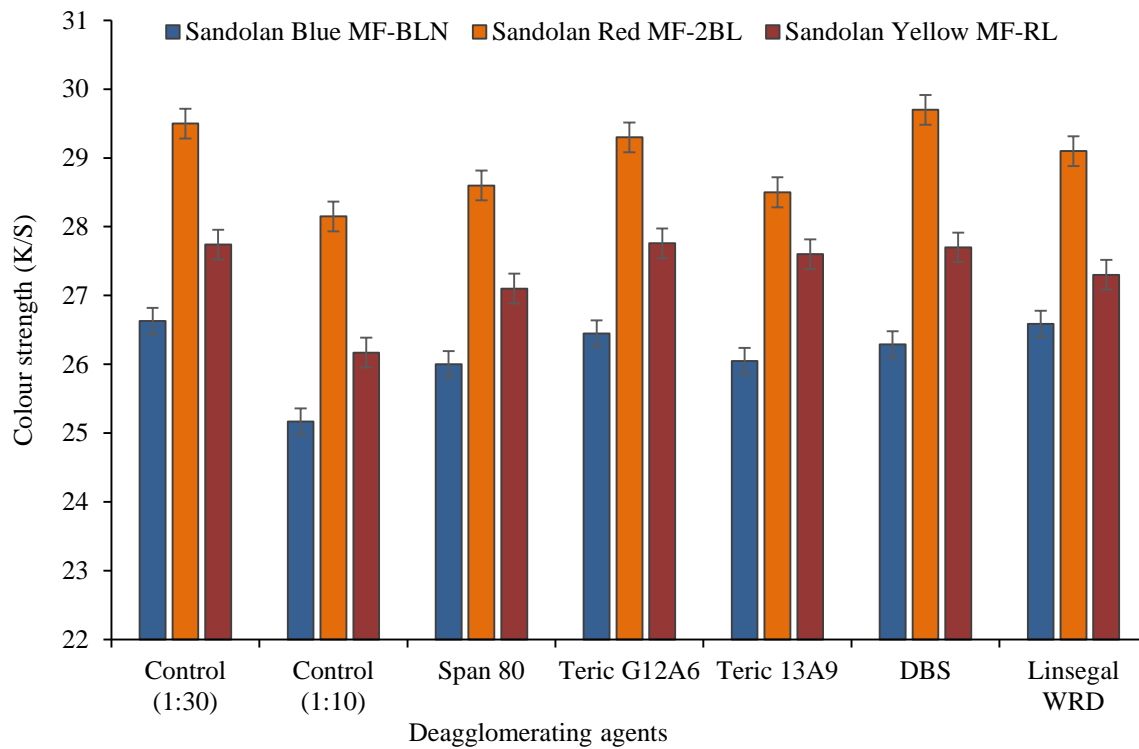
**Fig. 2.** Effect of various auxiliaries on the size of agglomerated dye particles for Sandolan Blue MF-BLN. a = control; b = Span 80; c = Teric G12A6; d= Teric 13A9; e = DBS; f = Linsegal WRD.



**Fig. 3.** Effect of addition of various surface active agents on the size of agglomerated dye particles for Sandolan Red MF-2BL. a = control; b = Span 80; c = Teric G12A6; d= Teric 13A9; e = DBS; f = Linsegal WRD.

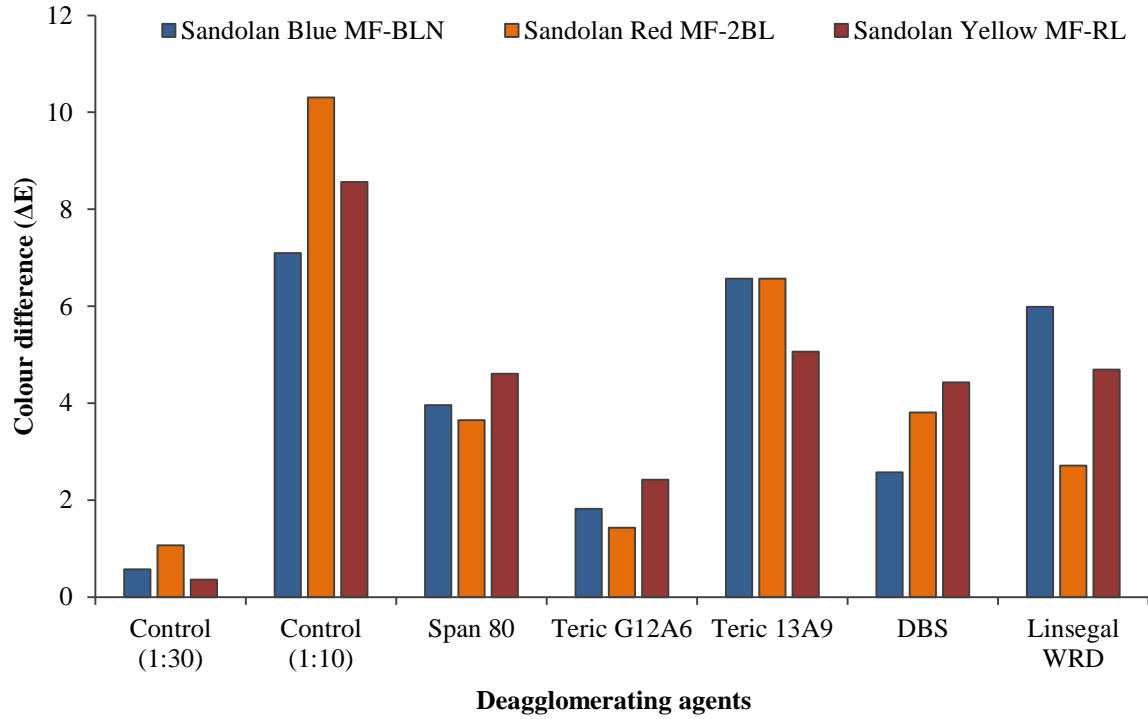


**Fig. 4.** Effect of addition of various surface active agents on the size of agglomerated dye particles for Sandolan Golden Yellow MF-RL. a = control; b = Span 80; c = Teric G12A6; d = Teric 13A9; e = DBS; f = Linsegal WRD.

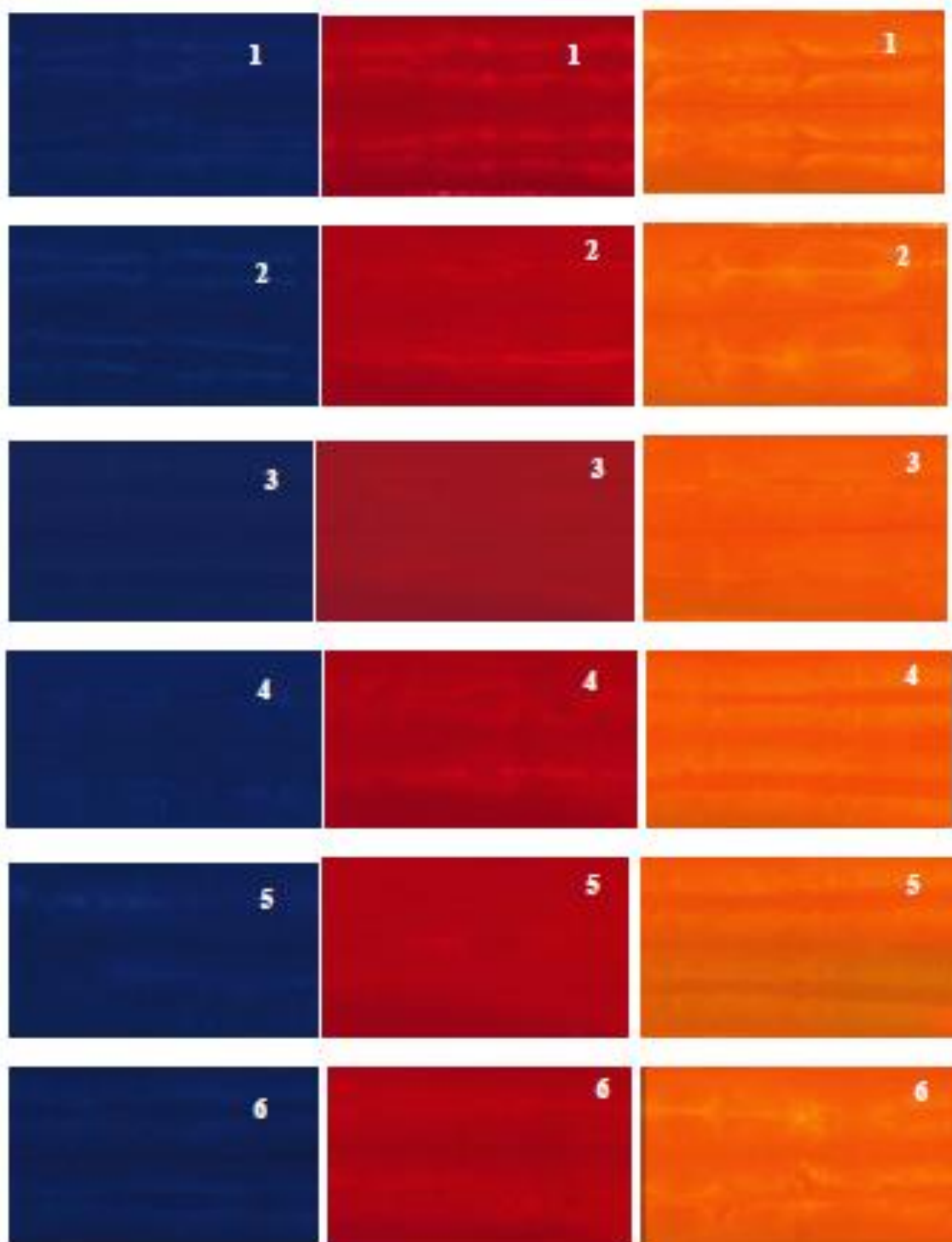


**Fig. 5.** Effect of addition of various agglomeration preventing agents on the colour strength of the wool fabric samples dyed with three acid dyes.





**Fig. 6.** Colour difference produced in dyed samples dyed in the presence of various dye agglomeration preventing agents.



**Fig. 7.** Optical images of wool fabric samples dyed with Sandolan Blue MF-BLN, Sandolan Red MF-2BL and Sandolan Golden Yellow MF-RL dyes in the presence of various dye agglomeration preventing agents. 1 = Control; 2 = Teric 13A9; 3 = Teric G12A6; 4 = DBS; 5 = Linsegal WRD; 6 = Span 80.

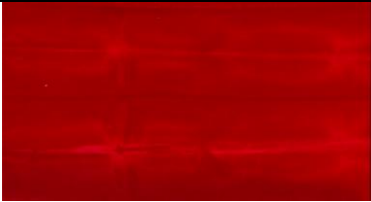
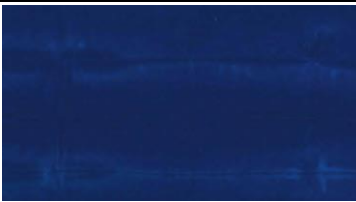
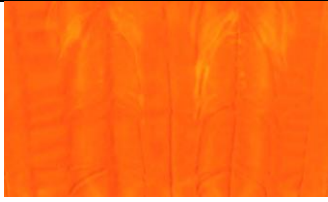





**Table 1.**

*CIE L\*a\*b\** values of wool fabrics dyed with Sandolan Red MF-2BLS, Sandolan Blue MF-BLN and Sandolan Yellow MF-RL dyes in the presence of various dye agglomeration preventers.

Dye agglomeration preventers	<i>CIE L*,a*,b*</i> values of fabric			<i>h</i> <sup>o</sup>	<i>CIE L*,a*,b*</i> values of fabric dyed			<i>h</i> <sup>o</sup>	<i>CIE L*,a*,b*</i> values of fabric	
	dyed with Sandolan Red MF-2BLS				with Sandolan Blue MF-BLN				with Sandolan Yellow MF-RL	
	<i>L*</i>	<i>a*</i>	<i>b*</i>		<i>L*</i>	<i>a*</i>	<i>b*</i>		<i>L*</i>	<i>a*</i>
Control (1:30)	33.73	51.02	28.80	29.44	23.62	0.53	-28.24	-88.92	52.98	40.15
Control (1:10)	37.08	52.09	26.97	27.37	26.91	-0.56	-30.37	88.94	58.65	35.51
Span	35.85	52.27	28.70	28.76	25.38	0.19	-29.06	-89.62	54.99	38.50
Teric 13A9	35.82	52.72	29.00	28.81	25.25	1.42	-29.89	-87.28	54.84	38.41
Teric G12A6	34.02	51.05	28.57	29.23	24.15	0.55	-27.88	-88.87	53.16	38.55
DBS	33.69	50.72	28.70	29.50	24.66	2.04	-30.31	-86.15	54.03	39.55
Linsegal WRD	35.63	52.98	29.67	29.24	23.92	0.53	-28.24	-88.92	54.24	40.06

**Table 2.**

Effect of TericG12A6 concentration on colour difference of wool fabric samples dyed with Sandolan Red 2BLS.

Applied dosage (% oww)	Sandolan Red 2BLS		Sandolan Blue MF-BLN		Sandolan Golden Yellow MF-
	Optical image	Colour difference ( $\Delta E$ )	Optical image	Colour difference ( $\Delta E$ )	Optical image
1		6.34		5.57	
2		1.43		1.82	
3		0.50		0.10	