Novel reducing agent for textile finishing

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In this article, a newly developed reduction agent is presented which can be used as an environmentally friendly replacement for hydrosulphite. Application in various processes is described.

State-of-the-art

For almost 100 years sodium hydrosulphite (or "hydro") has plainly been the reducing agent in textile finishing. The reason for its still unchallenged importance is most of all its universality and the price. Alternatives have recently been introduced being optimized with regard to ecology and handling. It mainly refers to dithionite mixtures, dithionite formaldehyd derivatives (hydromethyl sulphinates), nitrile otrimethyl sulphinites, thiourea dioxide, polyhydroxy compounds as well as hydroxyl acetone or reductones. Each one of these types proves to be superior in single aspects to the hydrosulphite. However, the fields of application are too limited; the advantages are unincisive with regard to environment and/or handling to actually replace the hydro in every respect. Thus, numerous problems are still occurring with these 2nd generation reducing agents with regard to dosing, storage, odor or dusting, but most of all with a high sulfur or COD input in the effluent.

A special inorganic chemistry could now be developed and introduced being indeed applied universally. Above all, it now offers considerable benefits with regard to ecology and handling compared to hydro and its former "competitors". Due to the increasing intensification in the German, EU and global legislation for the environment, particularly with regard to the sulfate, sulfate and COD input in effluent by direct inputs but also by increasing indirect inputs, this innovative reducing agent technology will certainly be established sooner or later as the so-called 'best available technology' in textile finishing.

New chemistry

The relatively new chemistry is based on an alkali-stabilized sulfur-free compound in mineralized form, which is put on the market in liquid form under the name Redutex BOR. This liquid formulation in combination with low viscosity, acceptable cold water solubility and high conductivity, allows the trouble-free application without the handling disadvantages known in self-igniting and lung-irritant powder systems as well as a comfortable manual and automatic dosing. The strong alkalinity corresponding to a 40 % caustic soda solution should, however, be considered and contact of the undiluted product with acids should be avoided. The ecological advantages of the product or product system compared with the reducing agent status quo are, on the one hand, that it contains only low amounts or no sulfite- and sulfate-generated sulfur at all and, on the other hand, it is mineralized, thus inorganic form (no COD input). According to extensive scientific studies, the inorganic salt resulting from the used reducing agent represents no hazard for human beings and environment namely for effluent, exhaust air and skin physiology. It should also be emphasized that the product is stable for a long period (far more than 1 year guaranteed storage life) without any loss of effects despite of its liquid formulation. The half-life period of its effect should be at least 5 years.

Areas of application

Even if the redox potential (compared to standard hydrogen electrode) does not considerably fall below a value of -900 mV at application conditions, it may due to its special effect still be used for all thinkable reductive applications, including vat dyeing; and this with a considerable saving potential not only with regard to chemicals but also to process costs. Compared to 'conventional systems' this means the advantageous multiple uses in the following processes (both discontinuous and continuous):
- Vat and sulfur vat dyeing
- Reductive intermediate and after-dyeing and prints on PET and PET blends
- Effluent discoloration
- Other reductive processes in the textile industry like machine cleaning, stripping of CO dyeing, reductive pre-treatment, sulfur dyeing, vat printing, desulphurization of CV or garment washing (stone-wash), dechlorination, etc.

The mode of application in different processes varies (Fig. 2). Whereas the product used as redox buffer in vat dyeing with catalyzing and stabilizing effect does not replace but clearly reduce hydro, it may be used in machine cleaning and reductive cleaning solely with alkaline solution.

A combination with an additional auxiliary (Redutex RAP) is recommendable for other processes, particularly for the reductive cleaning of PET and blends in the cooling dye bath not only continuously but also during effluent discoloration. It should be used with factor 10 compared with Redutex BOR and guarantees maximum effects and a neutral pH-value.

Compared with hydrosulphite, Redutex RAP is a compound with a clearly reduced sulfur content, which means a sulfur relief of approx. 40 % in the effluent. The same applies to Redutex BOR plus hydro in vat dyeing which results in a respectively reduced sulfur input.

Fig. 1 Properties of this novel reducing agent
If applied only with alkaline solution there is no sulfur input at all.

Reductive cleaning of PET dyeing and prints
Apart from Redutex BOR the use of the auxiliary Redutex RAP a relatively low-sulfur commodity at a ratio of 1:10 is important. This results in a pH-value of 7 advantageous for the goods and the process steps (Fig. 3) as well as in a considerable activation of Redutex BOR allowing minimum amounts in comparison with hydro or hydro derivatives.

Compared with thiourea dioxide the effect of Redutex BOR is about twice as strong, which also applies to other thiourea dioxide applications. This system is optimal for jet dyeing, particularly if applied in the cooling dye bath.

Compared with other reductive, sulfur-based systems possibly on the basis of the stabilization in the acid, cooling dye bath, the amounts of Redutex BOR to be used are considerably lower.

Due to an intended minimizing of oligomers such a process is, however, not optimal for machine dyeing; an alkaline reductive cleaning either alone with Redutex BOR or activated with the system BOR and RAP is recommended in this case.

Compared with conventional hydro applications this neutral, highly active and stable system in the continuous range, also referring to the very demanding intermediate or after-cleaning of PET/ cellulose thermostables or PET printing, allows a working method being much more economic and safer. Thus, in view of the unnecessary neutralizing processes and the lower amounts of application of Redutex BOR (compare with hydro) much smaller plants can be run or the working process can be carried out much faster on existing plants.

This results not only in a cost saving for chemicals but also in a cheaper process and an increased productivity respectively. Furthermore, the state of the vat is more stable and the feeding problem is minimized. After all, the automatic dosable liquid formulation of the product is of considerable advantage particularly for the continuous application.

Vat dyeing and sulfur vat dyeing
The capacity of Redutex BOR as a catalyst with redox buffering and stabilizing properties can be used here apart from hydrosulphite. The additional use of very low amounts of Redutex BOR in general allows a reduction of the usual amount of hydrosulphite by 40 ± 10 % without significant deviation of the coloring results.

This applies not only for the discontinuous (exhaust method) but also for the continuous process (pad steam dyeing). The lower the atmospheric oxygen the higher is the risk of stoppage. Apart from this saving, the state of reduction of the vat is equally good or better (in the continuous process the pad liquor stability) and the result in depth of shade and the rub fastness is even improved in most cases. This effect can be explained by a stabilized redox potential (Fig. 4).

The system immanent stabilizing also enables reduced amounts of usual protection agents against overreduction such as sodium nitrile or glucose with sensitive indanthrene types, as well as a substitution of hydroxyl methyl sulphimates by the lower-priced (and reduced quantity by 40 %) of hydrosulphite for vat HT dyeings.

The latter is particularly important in the area of yarn, most of all if it refers to regenerated cellulose dyeing (in the form of filaments).

Effluent discoloration
Especially in this field there seems to be a great future demand for new but simple technologies. Not only the German and the EU but even the international environmental legislation is tightened continuously and increasingly regulates the residual color of the effluent. In the meantime, this refers not only to the direct effluent drain in natural waters but at least locally also for companies indirectly draining effluent. This may lead to serious problems, not only for reactive dyes.

Major investments in superior cleaning technologies like wet oxidation, membrane filtration, electro flotation, etc. are only profitable for simultaneous recycling but not for a 100 % discharge. On the other hand, the no conventional and no longer up to date techniques of flocculation have to be considered as not specific for pure decoloration. Too much problematically discharchable sludge is produced and the treated water is additionally contaminated by electrolytes and/or polyquaternary ammonium compounds with rather high water toxicity.

Particularly in these cases, and due to the fact that especially the problematic reactive dyes are sensitive to reductive decoloration, the use of a cold water efficient reducing system is advantageous. The usual powdery systems are difficult to dose, whereas the usual liquid sys-
tems are not efficient enough here. Furthermore these systems contribute either to additional COD or sulfur in treated waste water. The system BOR/RAP however does not consist of all these disadvantages, apart from a considerably reduced sulfur contribution.

This system is well suited both for low colored and even more for high colored waste water with low application amounts and without large investments in plants. No sludge occurs and the metering with pumps, e.g. from containers is easily feasible.

At room temperatures the decoloration effect of this system is already fast, irreversible and redundant. Nevertheless the concentration of sulfite and sulfate ions does not exceed the critical concentrations for biological effluent treating plant or the concrete pipes respectively. Depending on the composition of the effluent (dye chromophor types and concentrations) this target is achieved with very low amounts of Redutex BOR besides Redutex RAP. The flow rate of the dosing pumps to be adjusted are easily calculated on the basis of the dose, evaluated by lab pretrials for total decoloration and the flow rate of waste water.

Dose [l/m²] x waste water flow rate [m³/h] = flow rate of dosing pump [l/h].

In most cases the decoloration is successful already at low temperatures and within short reaction time of less than 5 min. Actually the usually higher waste water temperature (particularly in case of treatment immediately after draining of liquors) is still improving the efficiency of irreversible decoloration.

The realization of the BOR/RAP system in (already existing) plants is very easy and only requires a minimum of effort and additional investment. However it has to be considered that both products have to be dosed separately into the decoloration basin or tank respectively and should be positioned near by the waste water feeding pipe to achieve maximum decoloration success. If both products were mixed directly (e.g. in high concentrations within a mixing pipe) an exothermic reaction would occur, which could cause damages due to spontaneous overheating.

Other reductive applications

Apart from the described applications many other fields of application exist. However those applications are either less important for the textile industry or do not comprise that economic saving potential compared with the "conservative" reducing agents.

For the cleaning of dyeing machines just 0.5 ml/l Redutex BOR besides caustic soda and possibly machine cleaning surfactants/solvents are enough for optimum effect. Concerning stripping of dyeing the product has proven to be successful particularly for CO dyeing with direct and reactive dyes. A positive by-effect for this application is the matter of fact that a subsequent neutralization due to the absence of core alkali may be avoided.

Outlook

There are still some "white spots" on the map of textile industry, where the application of the described system has not be introduced. Concerned are the vat printing (one phase), the sulfur dyeing (apart from sulfur vat dyes which may be treated in the same manner than vat dyes) and the indigo dyeing. But for nearly every other application of reducing system in the textile industry the new reducing chemistry has been introduced as an interesting and proven alternative to classical systems like hydrosulphite or thiourea dioxide.

Currently comprehensive trials are under way, both in the lab and in production. In many cases the theses are less a question of non feasibility for those applications but much more a question of lack of investigations and consolidated/comprehensive trial results in these fields. Resuming this new chemistry may be considered as the reducing system, which at the moment is the most environmentally friendly one, at least which concerns the proven and universally applicable systems. Other modern and interesting techniques with high ecological concern, such as the electrochemical processes (electrolysis) are not yet at this stage of practice realization, at least not in that universal manner. Furthermore, unlike the system BOR/RAP, the electrochemical methods for instance require new investment in new facilities and plants respectively.

Redutex BOR, Redutex RAP = registered trade names