Nylosan S – A High Fastness alternative for the Dyeing of Wool and Nylon Fibers.

The development of a New Dyestuff Class.

Slide 1

Introduction

The need for improved domestic and processing wet fastness combined with the effects of finer, duller nylons means the dyer is constantly searching for optimum techniques to meet these fastness demands. Such demands are not just restricted to the synthetic fibers.

Slide 2 – Microfibres

Slide 3 - Titer

The superfine long haired fibers such as mohair cashmere, alpaca, vicuna etc also offer similar problems of poor build up and subsequent unsatisfactory wet fastness.

The range of products available for these amine fiber types is of course well documented - a brief summary being

Slide 4 – All Dyes dye Nylon

Disperse – very limited fastness
Equalising – dood leveling/moderate wet/good lightfastness
Neutral – good wet fastness(with suitable aftertreatment)
Milling – good wet fastness – poor combinability
Premetalised – generally very good wet and light fastness
Chrome mordant (wool) – good leveling, good wet fastness but poor perborate fastness
Reactive – very good wt fastness, limited build up on PA
Sulphur – exceptional wet fastness but limited to black

The advantages/disadvantages of each class are well known but suffice to say an increase in fastness usually leads to a decrease in migration which can lead to application problems. The enviromental problems of heavy metals (both in effluent and on fiber) suggests that chrome dyes on a global basis will be obsolete within a few years.

Reactive Dyes on wool of course is not a new concept and their use has grown particularly rapidly over recent years due to the decline of the mordant species. They are particularly useful for deep bright shades but ultimately their success depends not only on their degree of fixation but also on their ease of clearing of unfixed dyestuff. Whereas all fiber forms can be dyed with this class there are potential problems in each case.

one due to the damaging effects to the fibre.

Slide 5 – Weakness of Reactive on Nylon

Reactive Dyes on Nylon is also not new but the problems of dyestuff yield, blocking in combination and barré effects is well documented. The cause of these three problems has one common denominator – the limited number of available free amino groups associated with the degree of dyestuff sulphonation (necessary for dyestuff aqueous solubility). A removal of these groups greatly enhances yields and reduces the blocking effects, but unfixed dyestuff has proven difficult to clear resulting in only moderate wet fastness. (Procinyl – ICI).

More recent attempts at using reactive dyes on nylon have included the use of a functional amine to impart increased dyeability.

Technical Requirements – as demanded of a new dyestuff – to satisfy the dyer and dyestuff supplier alike

Clariant has for a long time recognized the need for a dyestuff range to satisfy the demands set by polyamide micro-fiber (and the long haired natural fibers) and has recently introduced three new Nylosan S dyestuffs (Orange, Red and Navy) which we believe meet the modern day demands of the dyer ,the retailer and the consumer. All are new patented chemistry. The technical requirements (from a dyers perspective) for any dyestuff are:

Slide 6 – Technical Requirements to satisfy the dyer
Polyamide

Build up –
Fastness –
Combinability.
Economy –
Ease of Application
Health and Safety/ Ecological aspects in manufacture
Health and Safety in manufacture and in Handling.
Application – effluent discharges
Article use and disposal
Brilliance of Shade.

Requirements from Retailers/Eco Groups/legislation
Slide 7 - Requirements of Retailers, Enviromental Agencies/Consumer etc

Metal Free – Although a demand for metal free is not always specified by chain stores, the move in this direction is clear. The Eco label groups do make such demands and in many cases is a pre-requisite. The issue of heavy metal (even though covalently bound) should still be of concern to us all, be it relating to effluent in application or ultimately disposal after use. Is the future of the premetalised dyestuffs following the same path as the mordant dyes and if so how long before they meet the same destination?

Economy – Specific to the retailer. Whereas a need is recognised for high fastness, any cost increase must be measured against benefit.

Requirements of the Consumer
Color fastness – So as not to color contaminate other goods during washing.

Color Retention – The article to maintain its color after 20 30 or even 50 washes. This is particularly relevant to lingerie.

Economy – as customers, none of us want to pay more unless we can see an obvious benefit.

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The new elements are:
Slide 8 – The Nylosan S range

Nylosan Orange S-3R
Nylosan Red S-3B
Nylosan Navy S-3G

And these compliment the existing elements of:

Nylosan Yellow S-L
Nylosan Red S-GS
Nylosan Red S-B
Nylosan Blue S-3R

We shall now look at these new dyestuffs and assess the properties we believe are necessary for a new dyestuff range.
pH dependence
Slide 9
Ideally conditions of dyeing should produce the desired affects without any detriment to the fiber. In the case of wool, dyeing is preferably carried out at a pH in the iso-electric region which in practice is about

pH 4.5 and on nylon at pH 4.5 and upwards. (Lower pH levels have a profound reduction on light fastness).

In the design of a high fastness acid dyestuff, high affinity for the fiber is obviously important but only under the ideal conditions (ie. those of dyeing). For example, if a dyestuff has strong attractions for a fiber in alkaline conditions (ie. washing) then what is removed (equilibrium) in an alkaline liquor, will also stain adjacent white fiber.

This is particularly the case with the unsulphonated pre-metalised dyes whose attraction for the fiber is independent of pH.

Furthermore, if the dye in the dye liquor has only low fiber affinity in mildly alkaline conditions the rate of strike can be controlled by the pH function. Once on the fiber the inherent attractions come into play and the stronger such forces are, the higher the wet fastness. Planarity increases affinity in dyeing but also encourages cross staining in cellulosic blends and staining of cellulosic fibers in wash tests.

In summary, for optimum results the new acid dye must show:

High affinity under ideal dyeing conditions (pH 4.5 – 6.5)
Strong physical dye fiber bonding
Low affinity for fibres in alkaline aqueous medium
Have limited planarity

On polyamide
Slide 10 – Build as SD diagram
As we can see from the illustration , Nylosan S show limited neutral affinity but under the ideal acid conditions high exhaustion is achieved. Furthermore when we examine the build up we can see that Nylosan S achieves in excess of 8 x SD (on this nylon quality).
Slide 11 - Build of Orange/Red/Navy

On superfine wool fibres
Slide 12 – Orange/Red /Navy @ 2, 4, 6 SD
We can see the exceptional build up on Alpaca at 2, 4 , and 6x SD accompanied by outstanding wet fastness with the elements

Yellow S-L
Orange S-3R
Red S-3B
Navy S-3G

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Wet Fastness
Slide 13 Fiber Kinetic

Combined with high build up, the essential need of a dye range is high wet fastness. In the case of synthetic fibers, the level of fastness attainable is very heavily dependant on the fibers' characteristics. A fiber with rapid dye uptake compared to a slow dyeing fiber (kinetics) obviously shows poorer wet fastness than those fibers which have a much slower dyeing rate (easy in, easy out). With micro-fiber, the high surface area means a very rapid strike rate (absorption) and likewise a very rapid desorption in subsequent wet treatments.

Our objective was to produce dyes with high wet fastness – comparable at least, to that obtained with the highest wet fast premetalised dyestuffs ideally, without the need for after-treatment.

One possibility to increase fastness is to increase molecular size.

The concept of 'super-large' molecules to achieve high fastness is of course not new, but some of the potential negative aspects of this are listed as follows:

Slide 14 Superlarge molecules

'Superlarge' molecule	Leads to	Results in

High Molecular weight	Fiber sensitivity	Barré Dyeing
Polyazo	Increase conjugation	Dark (Brown/navy etc)shades
	Poor stability	Hydrolysis/Reduction
Metalised	Increased conjugation	Dull shades/ecology
Planar	High cellulosic affinity	Poor wash Fastness
	Aggregation	Precipitations
Degree of sulfonation	Fiber sensitivity	Barré
	Blocking	Poor reproducibility
Small chromophore	Poor tinctorially	Weak Dye/cost
(+ hydrophobic chain)	Foaming	Substrate flow/cavitation

Three examples of the variation in molecular weight based on anthraquinone chemistry , their dye classes and resultant fastness (on coarse nylon) are as follows (2/1 SD):

Slide 15 – Molecular weight and effect on wet fastness

CI Color Index	Class	MW	Wash Fastness		Alk Persp. Fastness	
			N	PA	N	PA
Acid Blue 40	Leveling	c. 460	2.9	1.7	4.5	1.1
Acid Blue 80	Milling	c. 650	4.3	4.9	4.7	2.3
Acid Blue 127	Super-milling	c. 820	4.3	2.5	4.4	4.7
Nylosan Blue S-R			4.6	4.9	4.6	4.9
Nylosan Navy S-3G			4.9	4.9	4.8	4.8

In the case of Acid Blue 80 what we see is that the increase in molecular weight brings about a dramatic improvement in wash fastness but the dyestuff still migrates in the perspiration test and the increase in molecular weight with Acid Blue 127 brings about no migration in the perspiration test and thus no staining, but the neutral affinity is increased and staining of nylon results in the wash test. Nylosan S shows virtually no staining in either test.

Slide 16 – A Fastness comparison of leveling/neutral/Milling and Nylosan S

A further evaluation of some commonly used acid yellow/orange and red dyes shows the possible wet fastness levels compared with Nylosan S:

Acid Yellow 199	Leveling	3.7	4.8	4.7	2.0
Acid Orange 676	Neutral	4.1	3.6	4.7	3.7
Acid Yellow 218	Milling	4.9	4.9	4.9	3.6
Nylosan Yellow S-L		4.9	4.9	4.9	4.9
Nylosan Orange S-3R		4.4	4.7	4.9	4.7
Acid Red 57	Leveling	3.5	2.3	4.8	1.3
Acid Red 299	Neutral	4.2	3.1	4.6	3.9
Acid Red 111	Milling	4.7	4.7	4.9	3.6
Nylosan Red S-3B		4.7	4.8	4.7	4.7

However on 91/9 PA/PU (1.15 d.tex) we see the need at 3 x SD for aftertreatment with Nylofixan HF

Slide 17 - Orange S-3R on PA/PU.

Slide 18 Red S-3B on PA/PU

Slide 19 – Navy S-3G on PA/PU

If we make a comparison against commonly used mono- sulphonated premetalised dyes we see a considerable improvement in wet fastness with Nylosan S.

Slide 20 – Lanasyn combinations v Nylosan S

On untreated wool we see also exceptionally high wet fastness levels not only to alkaline perspiration and washing but also to the processing fastness test – hot water, milling, decatising, overdyeing, sulphite setting.

Slide 21 – Orange S-3R on Wool gab
Slide 22– Red S-3B on wool gag
Slide 23 – Navy S-3G on wool gab

Combinability - polyamide

As already mentioned, large, non-metalised molecules of the milling dye class tend to be disulphonated. This degree of ionicity coupled with molecular size leads to molecular hinderance which in turn leads to dyestuff blocking and limited build up – particularly in combination. It is simple – the dyestuff with the highest affinity will block the available sites first and the dyestuff which is slower to dye has no sites to attach itself to.

Slide 24 – Strike rates – fixed pH – anionic leveler – Lyogen CN

Slide 25 – Strike rates – acid donor (Opticid VS) – anionic leveler – Lyogen CN

Nylosan Yellow S-L }	Good combinability
Nylosan Red S-3B }	Good light fastness
Nylosan Blue S-R }	
Nylosan Yellow S-L }	Good combinability
Nylosan Red S-3B }	Moderate light fastness
Nylosan Navy S-3G }	Economy
Nylosan Orange S-3R}	Moderate combinability
Nylosan Red S-3B }	Good light fastness
Nylosan Blue S-R }	
Nylosan Orange S-3R}	Excellent combinability
Nylosan Red S-3B }	Moderate light fastness
Nylosan Navy S-3G }	

Tonally the rate of strike is generally very good and even in the worst case can be considered better than some traditional premetalised combinations. The variation in dyeing method is also seen to have some positive or negative effects on the tonal strike.

The importance of this even strike cannot be emphasized enough – particularly when dyeing difficult substrates in difficult circumstances (eg. Flat woven polyamide fabrics with high kinetics on the jig which can lead to edging or side to side variation and knitted polyamide fabrics with low kinetic on the beam which can lead to in to out variations)

Combinability – wool

Due to the poor coverage of tippy wool (ie light exposed) by Nylosan Blue S-R, we are restricted to full shades based on Nylosan Navy S-3G.The following combinations:

Slide 26 – S-L/S-3B/S-3G
Slide 27 – S-3R/S-3B/S-3G

Nylosan Yellow S-L
Nylosan Red S-3B
Nylosan Navy S-3G

Nylosan Orange S-3R
Nylosan Red S-3B
Nylosan Navy S-3G

give again excellent combinability. The limitations on light fastness in paler shades essentially means these combinations are restricted to full shades.

The coverage of loose stock wool by both these combinations is excellent.

Slide 28 – Loose wool – Nylosan S compared to Milling/Premet

Economy

This is best determined by tinctorial strength (assessed as Standard depth) multiplied by the actual cost of production or determined selling price.

High material cost due to complications of chemistry and/or poor yields
Tinctorially weak product caused by the chemistry used

Ease of application

The modern organic dyestuff industry is well over 100 years old. Many interesting developments have occurred in this period, but largely the application methods have rarely changed – that is, dyeing of the substrate is carried out from an aqueous medium, some chemicals are added to assist in levelness or dye uptake etc., the dyebath is usually heated to reduce dyeing time and allow for better dye/ liquor/fabric flow and rinsing (soaping) is essential following dyeing to achieve optimum fastness. It is a relatively simple technique for all dyes on all fibers. The more complicated the processing route the more possibility of errors. It is important we believe, that this relatively simple technique should remain as such.

We propose four dyeing methods for polamideto cover most possibilities:

Slide 29 – Dyeing Methods on PA – jet/winch/hank/garment
Slide 30 – Loose stock/tops/package/beam
Slide 319 – Heavy Barré material
Slide 32- jigger

1. Fabric and liquor movement – Hank/Jet/Winch/Paddle/Rotary Drum
2. Circulating systems – Loose stock/Tops/Package/Beam
3. Fabric and liquor movement – Barrè -Jet/Winch
4. Jig Dyeing

Correction of faulty dyeings should also not be overlooked. On polyamide, unlevel Nylosan S dyeings can be corrected by reheating to the boil under alkaline conditions (c. pH 9 -10) are re-exhausted by reducing the pH with acid donor. This technique is the same as is used for any other milling class of dyestuff but with Nylosan S the conditions tend rto be a little more sever due to the high affinity).

Slide 33 – Migration and exhaustion of Nylosan S on PA
Slide 34 – Circulation Dyeing
Slide 35 Dyeing Methods on wool – Piece Dyeing
Slide 36 – Long haired fibers
Slide 37 Clearing

On wool, the re-leveling conditions are restricted a little by the wools' sensitivity to alkali at high temperatures. Successful reduction of depth is achieved at pH 8 at 80 deg. C. with addition of a cationic leveler. Topping up of the shade in fresh liquor is preferred.

Slide 38 – Stripping effect of pH/Lyogen NH on wool

Conclusion

Slide 39 – Nylosan S - conclusions

With the new patented Nylosan S elements we believe we have developed a completely new dyestuff class – a ‘super’ super milling if you like. These new dyes compliment the already existing range of Nylosan S and achieve unprecedented levels of

Build up
Combinability
Fastness

Employing simple application and correction techniques and are
Metal Free
Moderate to bright shades
Show economy similar to that of the mono-sulphonated premetaslised dyes

and
Comply with probable future legislative requirements

on wool (including the superfine types) and polyamide microfibers alike.
We believe we have created an answer to some of the outstanding issues faced by the dyer and retailer with Nylosan S and of which we shall further extend the color range in the future .