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Substitute products for urea in application of reactive dyes to cotton fabrics

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Caprolactam, PEG 400 and PEG 600 have been identified as partial or complete substitutes of urea in the dyeing and printing of reactive dyes on cotton fabrics. It is observed that the caprolactam in many reactive dyes can replace urea while PEG 400 and PEG 600 are effective for replacement to the extent of about 50% of the optimum concentration of urea required for fixation.

Keywords: Caprolactam, Cotton, Dyeing, Polyethylene glycol, Printing, Urea

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1 Introduction

During dyeing/printing of cellulosic fibres with reactive dyes, the addition of urea to the pad-liquor or print-paste is recommended and it is considered by textile printers that such addition results in brighter and more level prints. Specific action of urea in continuous dyeing or printing with reactive dyes is highly complex and different opinions have been expressed to explain the results obtained under different conditions of application regarding the role played by urea[1-8]. Main functions of urea during continuous application of reactive dyes have been found to be the increasing solubility of dye in reaction medium, controlling evaporation of water during drying and swelling of cotton, thereby facilitating the dye-fibre reaction.

However, when dyeings or prints containing urea are washed-off, the urea is decomposed easily producing nitrogenous compounds which accelerate the growth of algae, resulting in undesirable stream pollution. In view of the fact that the environmental regulations regarding stream pollution are becoming more rigid, different approaches for elimination or replacement of urea in dyeing and printing have been adopted. Some of them are given below:

- Partial or complete substitution of urea by alternate products[8-10].
- Controlled mechanical application of moisture before sample enters in steamer[11].
- Controlled drying of urea-free printed fabrics prior to steaming[12].
- Adoption of two-stage printing through flash ageing.
- Replacement of sodium alginate by synthetic thickeners.

In the present study, different dye-solublising agents and hydrotropic substances have been examined as chemical substitutes for urea, whereby simple substitution of a more environment-friendly product could be effected.

2 Materials and Methods

2.1 Materials

2.1.1 Fabric

Mills desized, scoured, mercerized and bleached cotton fabric (warp count 30s; weft count 30s; ends/inch 96; and picks/inch 60) was used in the study. The procedures followed for desizing, scouring, mercerizing and bleaching were as follows:

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Desizing

Amylase enzyme	:	0.8 g/L
Calcium chloride	:	1 g/L
Sodium chloride	:	1 g/L
Duration	:	4 h
pH	:	7.0
Machine	:	JT-10 (Jig)

Scouring

Sodium hydroxide	:	4 % owf
Wetting agent	:	0.5%
Temperature	:	95^{0}C
Duration	:	3 h
Machine	:	JT-10 (Jig)

Mercerization

Scoured fabric was mercerized with 300 g/L caustic soda.

Bleaching

H_2O_2	:	2% owf
Stabiliser	:	0.6 % owf
Wetting agent	:	0.3 % owf
Temperature	:	95^{0}C
Duration	:	2 h

Fabric was given hot and cold wash and neutralized with 0.5-1 g/L acetic acid at every stage of operation.

2.1.2 Dyes

Vinyl sulphone reactive dyes used were C.I. Reactive Yellow 15, C.I. Reactive Yellow 37, C.I. Reactive Orange 107, C.I. Reactive Orange 16, C.I. Reactive Red 35, C.I. Reactive Red 37, C.I. Reactive Violet 5, C.I. Reactive Blue 21, C.I. Reactive Blue 19 and C.I. Reactive Black 5.

2.1.3 Chemicals

Substitute products (laboratory reagent) used were cellosolve, glycerine, sorbitol, polycarboxylic acid, polyethylene glycol (200, 400, 600, 4000) and caprolactam.

2.2 Methods

2.2.1 Dyeing

2.2.1.1 Pad-dry-cure Method

Padding liquor consisted of following ingredients:

Dye	:	40 g/L
Urea or substitute product	:	20-80 g/L
Sodium bicarbonate	:	36 g/L
Water	:	904-844 ml
Total	:	1000 g

Fabric was padded on ERNST BENZ AG padding mangle with dye solution keeping an expression of 80%, dried at 80 °C and cured in Werner Mathis AG Drier Steamer at 140 °C for 90 s.

2.2.1.2 Pad-dry-steam Method

Padding liquor consisted of following ingredients:

Dye	:	40 g/L
Urea or substitute product	:	20-80 g/L
$NaHCO_3$	:	18 g/L
Water	:	922-862 ml
Total	:	1000 g

Fabric was padded with dye solution keeping an expression of 80%, dried at 80°C and steamed in Star Steamer at 100-103°C for 7 min.

2.2.2 Printing

2.2.2.1 Print-dry-cure method

Print paste consisted of following ingredients:

Thickening agent		
Sodium alginate, 8%	:	450 g/kg
Dye	:	40 g/kg
Urea or substitute product	:	10-100 g/kg
Resist salt	:	15 g/kg
$NaHCO_3$	:	25 g/kg
Water	:	460-370 ml
Total	:	1000 g

Fabric was printed, dried at 90°C and cured at 140°C for 90 s.

2.2.2.2 Print-dry-steam Method

Print paste consisted of following ingredients:

Thickening agent		
Sodium alginate, 8%	:	450 g/kg
Dye	:	40 g/kg
Urea or substitute product	:	10-100 g/kg
Resist salt	:	15 g/kg
$NaHCO_3$	:	20 g/kg

Water	:	465-375 ml
Total	:	1000 g

Fabric was printed, dried at 90°C and steamed at 100-103 °C for 10 min. Dyed or printed fabrics were washed with 5 g/L non-ionic detergent at 95°C for 30 min to remove unfixed dye.

2.2.3 Colour Strength Measurement

Colour strength (*K/S*) was calculated from reflectance measurements carried out on Macbeth Color Eye-7000A spectrophotometer using the following Kubelka-Munk equation:

$$K/S = [(1 - R)^2/2R]$$

where R is the reflectance; K, the absorption coefficient; and S, the scattering coefficient.

3 Results and Discussion

3.1 Substitution in Dyeing

It is known that the quantity of urea normally recommended for incorporation in pad liquor varies between 50 g/L and 60 g/L depending on the method of fixation adopted. However, this is not the optimum amount for maximum fixation of reactive dyes, and it varies from dye to dye and type of reactive system in the dye molecule. Therefore, in the present study, the optimum concentrations of urea required under given set of conditions have been obtained for each dye examined using pad-dry-cure and pad-dry-steam techniques. Subsequently, the effect of reducing this quantity progressively and replacing it by alternate substitutes without any adverse effect on the extent of fixation has been examined.

Table 1 indicates that in case of pad-dry-cure technique, the extent of fixation increases as the concentration of urea increases from 10 g/L to 80 g/L. With C. I. Reactive Orange 107 and Red 35, beyond 60 g/L urea concentration the fixation remains more or less the same while with C. I. Reactive Yellow 15 and Blue 19, the optimum quantity of urea is 80 g/L. In case of pad-dry-steam technique, beyond an optimum concentration (20g/L), further increase in concentration to 80 g/L results in a decrease in fixation or the extent of fixation remains the same. Such reduction in fixation is likely to be because of rupture of vinyl sulphone dye-fibre bond due to the combined alkaline action of urea and sodium carbonate from bicarbonate. However, with C. I. Reactive Blue 21, which is a metal-complex vinyl sulphone dye and has low reactivity to cellulose, the extent of fixation increases when the quantity of urea is increased from 20g/L to 80 g/L.

To evaluate alternate substitutes for urea in dyeing with vinyl sulphone reactive dyes, the main consideration has been given to the ability of substitute product to bring about effective solublisation of dye in the padding liquor and retention of sufficient quantity of moisture in the fabric during the curing stage where fixation of dyes takes place in case of pad-dry-cure application. Cellosolve, glycerine, sorbitol and polyacrylic acid were examined for partial substitution. However, it is observed that none of these products individually or in combination has been an effective substitute for urea, and the extent of fixation in every case is always less as compared to that obtained at optimum concentration of urea.

Table 1 — *K/S* values for vinyl sulphone dyes used in presence of different amounts of urea

Dye	*K/S* value										
	Pad-dry-cure						Pad-dry-steam				
	Nil[a]	10[a]	20[a]	40[a]	60[a]	80[a]	Nil[a]	20[a]	40[a]	60[a]	80[a]
C. I. Reactive Yellow 15	4.1	-	4.2	5.6	7.7	13.0	14.9	15.8	15.8	15.5	15.2
C. I. Reactive Orange 107	11.1	12.7	13.2	16.6	16.6	16.8	17.6	17.7	17.0	17.3	17.6
C. I. Reactive Red 35	7.8	8.5	8.5	9.8	12.1	12.3	15.2	17.1	17.3	15.6	15.1
C. I. Reactive Blue 21	-	-	-	-	-	-	18.2	16.9	19.1	20.6	21.3
C. I. Reactive Blue 19	4.7	4.5	4.9	7.4	7.4	9.1	9.9	11.0	10.1	10.2	9.6

[a]Urea concentration in g/liter

After intensive screening of several substitute products, three products have been experimentally identified as partial or complete replacement of urea in continuous methods of dyeing. These are polyethylene glycols (PEG) 400 and 600 and caprolactam.

To find out appropriate molecular weight polyethylene glycols, the PEG molecular weights ranging form 200 to 4000 have been examined at different concentrations as substitute for urea (Table 2). It is observed that the PEG 400 and PEG 600 show comparable fixation for C I. Reactive Orange 107, Red 35 and Black 5, while C. I. Reactive Yellow 15 and Blue 21 show lower colour value as compared to that observed at optimum concentration of urea in case of dyeing with continuous methods. Caprolactam at 60-80 g/L concentration shows fixation, for most of the dyes, equivalent to that observed at optimum concentration of urea, irrespective of the method of dyeing. Thus, PEG 400 and PEG 600 can replace urea partially while caprolactam can replace urea completely in case of continuous methods of dyeing (Tables 2-4, Fig.1).

3.2 Substitution in Printing

As mentioned earlier, three substitute products have been identified as partial or complete replacement for urea in the dyeing of cotton textiles with reactive dyes using continuous methods of application, viz. pad-dry-cure and pad-dry-steam techniques. It was, therefore, thought desirable to examine the feasibility of urea substitution by these three substitute products during printing with reactive dyes, as urea is used as dye-solubilising agent as well as a hydrotope in large quantities during printing.

Table 2 — *K/S* values for vinyl sulphone dyes used in presence of different molecular weight PEG

Product	Conc. of product g/L	*K/S* value				
		C. I. Reactive Yellow 15	C. I. Reactive Orange 107	C. I. Reactive Red 35	C. I. Reactive Blue 21	C. I. Reactive Black 5
Urea	Nil	7.5	12.6	8.0	10.7	25.6
	60	11.6	16.7	12.4	12.6	27.7
PEG 200	20	9.0	14.1	9.3	11.0	-
	40	9.9	13.0	9.4	10.6	-
	60	9.5	12.3	9.2	11.6	-
	80	8.6	10.9	8.9	11.1	-
PEG 400	20	10.0	16.3	11.3	10.4	27.1
	40	10.5	14.0	11.4	11.7	26.0
	60	10.3	12.9	10.0	11.1	22.4
	80	10.3	12.2	10.7	11.1	23.1
PEG 600	20	9.6	15.9	13.1	9.9	28.4
	40	10.4	14.2	10.6	9.9	24.3
	60	9.8	13.3	10.1	10.3	20.1
	80	9.5	12.2	9.4	10.2	17.8
PEG 4000	20	7.3	12.5	11.1	7.1	-
	40	7.1	11.5	10.4	6.4	-
	60	7.0	9.4	9.2	6.5	-
	80	7.0	9.3	8.0	6.4	-

Table 3 — *K/S* values for vinyl sulphone dyes used in presence of different molecular weight PEG at optimum concentrations

Dye	*K/S* value								
	Pad-dry-cure				Pad-dry-steam				
	Urea		PEG 400 (20 g/L)	PEG 600 (20 g/L)	Urea			PEG 400 (10 g/L)	PEG 600 (10 g/L)
	Nil	60 g/L			Nil	20 g/L	60 g/L		
C. I. Reactive Yellow 15	7.5	11.6	10.0	9.6	14.2	15.8	15.5	12.9	12.6
C. I. Reactive Orange 107	12.6	16.7	16.3	15.9	18.1	20.0	17.3	21.4	17.2
C. I. Reactive Red 35	8.0	12.4	11.3	13.1	16.4	17.1	15.6	17.3	20.2
C. I. Reactive Blue 21	10.7	12.6	10.4	9.9	18.8	16.9	21.6	19.9	17.7
C. I. Reactive Black 5	25.6	27.7	27.1	28.4	29.0	29.3	30.3	30.1	30.1

Table 4 — *K/S* values of printed samples produced with vinyl sulphone dyes in presence of different amounts of urea

Dye	*K/S* value											
	Print-dry-cure						Print-dry-steam					
	Nil[a]	10[a]	20[a]	50[a]	70[a]	100[a]	Nil[a]	10[a]	30[a]	50[a]	70[a]	100[a]
C. I. Reactive Yellow 15	2.2	2.2	2.1	3.3	7.2	14.8	25.1	24.5	25.0	25.0	26.7	25.8
C. I. Reactive Orange 107	-	4.2	6.4	12.3	21.2	21.4	26.3	25.7	25.2	25.3	25.5	24.7
C. I. Reactive Red 37	3.8	4.1	6.1	9.9	16.9	23.3	27.3	27.4	27.1	27.0	26.6	26.6
C. I. Reactive Blue 28	2.7	3.5	5.5	9.9	13.6	14.8	-	-	-	-	-	-
C. I. Reactive Blue 19	-	-	-	-	-	-	15.6	14.9	15.7	16.7	19.3	21.4
C. I. Reactive Blue 21	2.6	3.5	4.1	6.4	13.1	14.7	22.9	22.7	23.0	23.3	24.5	25.6
C. I. Reactive Black 5	-	11	15.2	21.6	25.1	25.2	-	-	-	-	-	-

[a]Urea concentration in g/L

In the first instance, the optimum concentrations of urea required for effective fixation of different reactive dyes by print-dry-cure and print-dry-steam techniques of application were determined. Once this quantity was determined, the effect of substitute products could be determined without any adverse effect on the extent of fixation.

Table 4 shows that in case of print-dry-cure technique, as the concentration of urea is increased from 70 g/kg to 100 g/kg, the colour value increases for C. I. Reactive Yellow 15, Red 37, Blue 28 and Blue 21 while with C. I. Reactive Orange 107 and Black 5, the increase in concentration of urea has practically no effect on the extent of fixation.

In case of print-dry-steam technique, with C. I. Reactive Blue 19 and Blue 21, the extent of fixation increases progressively as the concentration of urea in the print paste is increased from 50 g/kg to 100 g/kg print paste while with C. I. Reactive Yellow 15, Orange 107 and Red 37, the fixation remains more or less the same with or without urea. With later three dyes, the marginal decrease is observed in presence of urea (Table 4). This decrease is likely to be due to the increase in alkali content in the print paste as a result of combination of higher quantities of urea and

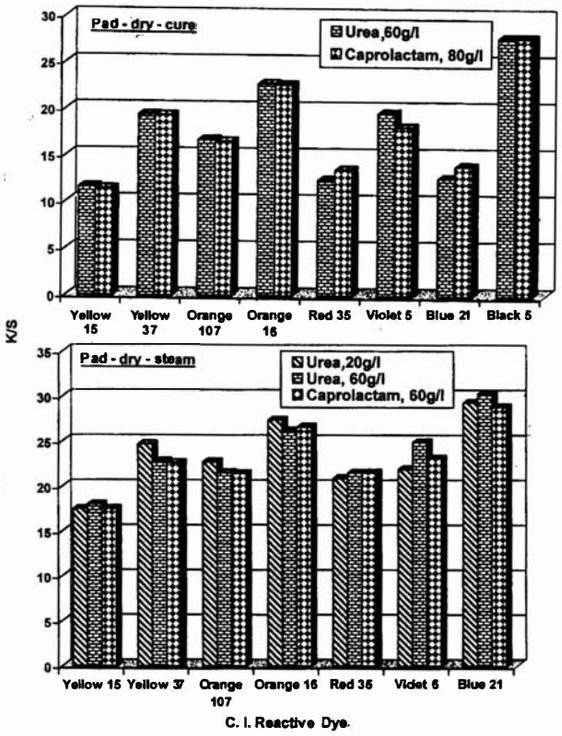

Fig. 1 — Reflectance (*K/S*) values of dyeings produced with vinyl sulphone dyes applied by continuous methods in presence of optimum concentrations of caprolactam

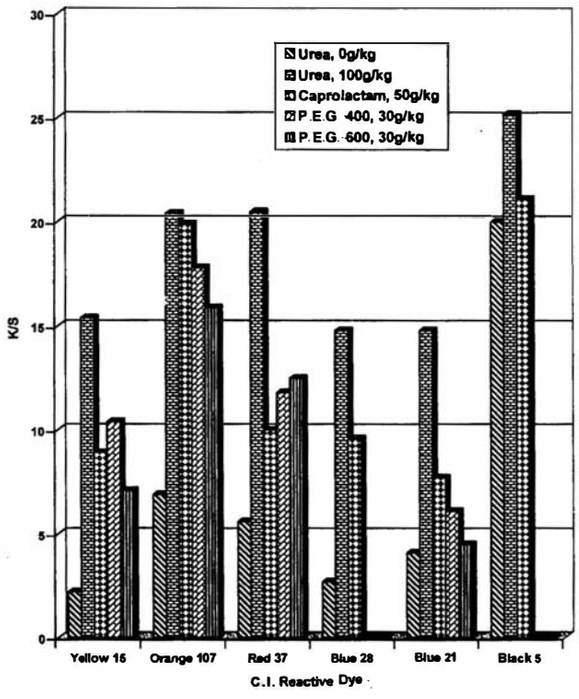

Fig. 2 — Reflectance (*K/S*) values of printed samples produced with vinyl sulphone dyes applied by print-dry-cure method in presence of different products at optimum concentrations

bicarbonate, which, in turn, may result in rupture of vinyl sulphone dye-fibre bond.

For studying feasibility of partial or complete substitution of urea, PEG 400, PEG 600 and caprolactam have been examined both for print-dry-cure and print-dry-steam methods. As these substitute products are acidic (pH 5.0-6.0) in nature, the compatibility with sodium alginate thickener was examined by viscosity measurement in Brookfield viscometer. The changes in viscosity of print paste in the absence and presence of dye show comparable results among the entire three substitute products individually and in combination with urea in comparison to the results obtained at optimum concentration of urea in the print paste.

Subsequently, the printing was carried out in presence of different substitute products and urea. The results indicate that in case of print-dry-cure method of fixation, it is not possible to substitute urea completely by any of the three substitute products when compared to the results obtained at optimum concentration of urea (100 g/kg) (Fig. 2). However, the dye fixation is always higher than that obtained in the absence of urea in print paste. In case of combination of urea (50% of optimum concentration) with the increase in concentration of each of the three substitute products, the extent of fixation increases. The optimum concentration obtained for both PEG 400 and PEG 600 is 30g/kg, while for caprolactam it is 50g/kg when used along with 50g urea/ kg print paste for comparable fixation (Fig.3). However, PEG 400 gives more or less comparable fixation for C. I. Reactive Yellow 15, Orange 107 and Red 37 while lower colour value is observed for C. I. Reactive Blue 19 and Blue 21, as compared to that observed at optimum concentration of urea. PEG 600 gives comparable fixation for C. I. Reactive Orange 107 and Red 37 and lower fixation for C. I. Reactive Yellow 15, Blue 19 and Blue 21 as compared to that obtained at optimum concentration of urea.

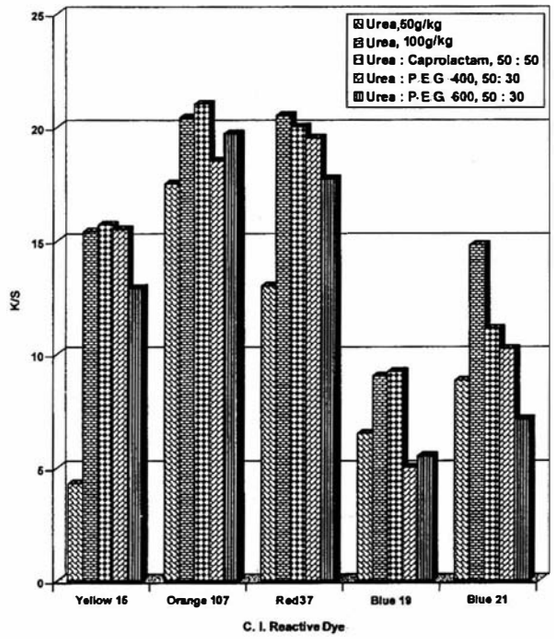

Fig. 3 — Reflectance (*K/S*) values of printed samples produced with vinyl sulphone dyes applied by print-dry-cure method in presence of different products at optimum concentrations and reduced quantity of urea

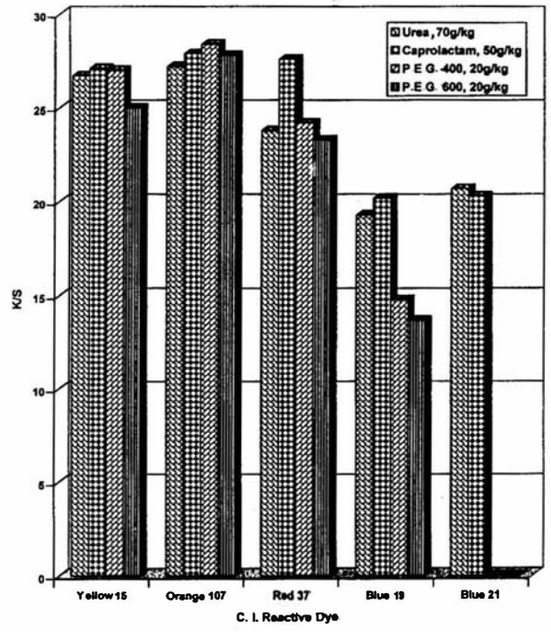

Fig. 4 — Reflectance (*K/S*) values of printed samples produced with vinyl sulphone dyes applied by print-dry-steam method in presence of different products at optimum concentrations

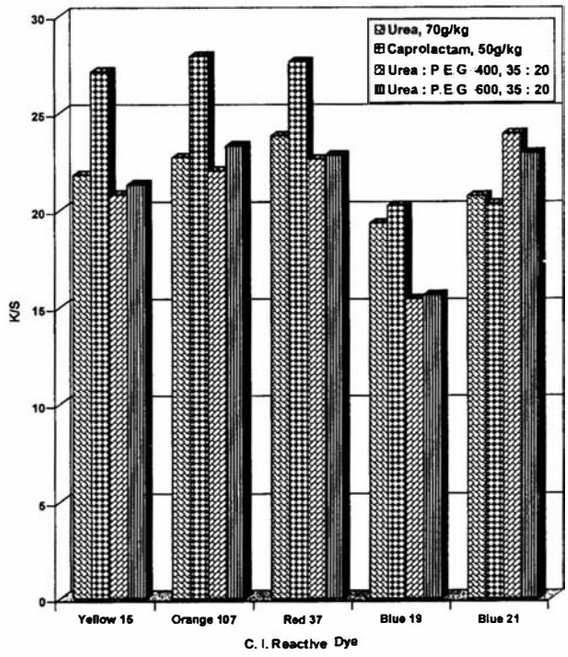

Fig. 5 — Reflectance (*K/S*) values of printed samples produced with vinyl sulphone dyes applied by print-dry-steam method in presence of different products at optimum concentrations and reduced quantity of urea

Table 5 — Biodegradability of urea and different substitute products

Product	Biodegradability after 28 days, %
Urea	15.5
PEG 400	64.5
PEG 600	70.9
Caprolactum	98.6

Caprolactam shows comparable fixation to that of urea for all dyes studied except C. I. Reactive Blue 21.

In case of print-dry-steam method of fixation, 50g/kg of caprolactam completely replaces urea for equivalent fixation obtained at optimum concentration of urea (70g/kg) for all the dyes studied (Fig. 4). PEG 400 or PEG 600 alone at 20g/kg in print paste gives colour value comparable to that observed using 70g/kg of urea (Fig. 4), except for C. I. Reactive Blue 19 and Blue 21. However, at 50% of optimum concentration of urea (35 g/kg print paste) and 20

g/kg PEG 400 or PEG 600, the fixation is comparable to that observed using 70g/kg urea alone (Fig. 5). In case of C. I. Reactive Blue 19, the presence of PEG 400 or PEG 600 gives marginally lower colour value as compared to that observed at optimum concentration of urea.

Biodegrability is calculated in terms of BOD/COD ratio. Results indicate that biodegradability of the substitute products is greater than that of urea (Table 5).

4 Conclusion

It appears possible to partially substitute urea by two specific types of polyethylene glycols and in some cases even complete substitution can be effected by caprolactam without much sacrifice in colour value of dyeings/prints. Products are biodegradable.

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