São Paulo - Brazil - May - 22nd to 24th - 2013
4th INTERNATIONAL WORKSHOP
ADVANCES IN CLEANER PRODUCTION
"INTEGRATING CLEANER PRODUCTION INTO SUSTAINABILITY STRATEGIES"

Reactive and Vat Dyestuff in the Dyeing of Cotton: A Review of Energy and Water Consumption, Ecological Analysis and Effluent Treatment

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Abstract

This study compared reactive dyestuffs and vat dyestuffs in the dyeing of cotton, evaluating the reuse of the effluent generated, the ecological costs, water and energy consumption. The experiments with vat dyestuffs showed slight advantage in ecological costs, generating less molecules of carbon dioxide than the experiments conducted with reactive dyestuffs, lower consumption of energy, greater possibility of reuse of treated effluent, which presented decolorization efficiency above 99% in all cases.

Keywords: *reacitve dyestuff, vat dyestuff, dyeing of cotton, ecological costs.*

1. Introduction

In the Brazilian textile industry, the dyeing and the finishing of knitted fabrics of cotton had a growth of 237,638 ton in 2008 to 267,196 ton in 2010, representing a growth of 11 %.[1] In addition, the textile sector is responsible for a large part of the economy of developed countries, as well as the main economic activity of some developing countries.[2]

All the products are bleached, dyed, washed or printed and need an average amount of 75 liters of water for every kilogram treated.[2,3] When these data are compared, there is an alarming increase in water consumption of approximately 2.2 million cubic meters in three years. Due to scarcity of water and the high costs of treatment, it becomes essential to search for alternative methods that allow the reuse of the effluent and, consequently, sustainability in the various processes of coloring.4 Therefore, the objective of this paper was to study the development of colors in cotton with two classes of dyestuff. Because of the event Cup FIFA World - Brazil, 2014, probably there will be an increase in the dyeing of the colors of the Brazilian flag, which are the Yellow (Pantone 120643), Green (Pantone 186024) and the Blue (Pantone 194035), these dyeing will be performed in tissues or in pieces made up of cotton, the main fiber used in current scenario of Brazilian clothing. These colors were developed analyzing the energy balances, fastness of the colors, ecological costs involved in dyeing processes and the possibility of reuse of water after a treatment of the effluent generated.

1.1. Reactive dyestuff

The reactive dyestuff is relatively easy to apply, has a good resistance to wet treatments and, in agreement with the Brazilian Association of the Chemical Industry (ABIQUIM), its use and trade account for 57% of all the dyestuffs used in Brazil.[5,6] A considerable amount of research on water treatment has been focused on the effluents originated from the dyeing with the kind of dyestuff, essentially for three reasons: firstly, fractions of the reactive dyestuff (10 to 50 %) are wasted during the process of dyeing (up to 0.6 g·L-1 can be detected in the effluent), because these dyes react not only with the fiber, but also with water; secondly, conventional effluents treatment, adsorption and aerobic biodegradation mainly, demonstrate inefficient for the complete elimination of many reactive dyestuffs; and thirdly, they also require a large amount of water during the washing process in order to remove the hydrolyzed dyestuff from the surface of the fiber.[7,8,9,10] The reactive dyestuffs used in this study were a bi-functional type vinylsulphone and monochlorotriazine (C.I. Reactive Red 195), a bi-functional type vinylsulphone (C.I. Reactivate Black 5) and two monofunctional type vinylsulphone (C.I. Reactive Blue 19 and C.I. Reactive Blue 21).

1.2. Vat dyestuff

According to Zollinger (1991), from all dyestuff for cellulosic fibers these are the ones that present the best levels of fastness.[11] The production of vat dyestuff in Brazil was approximately 22% of the total of 23,000 tons of all dyestuffs produced by Clariant in 2010. The vat dyestuff is insoluble in water and the dyeing with the kind of dyestuffs is based on the principle of conversion of ketones groups into sodium enolates groups by reduction in alkaline medium. This form is soluble in water and has a high substantivity to the cellulose. After the adsorption, migration and diffusion, the dyestuffs establish hydrogen bonds with the fiber. After the dyeing step, the dyestuff needs an oxidation in order to returns in the original form. All vat dyestuffs contains two or more groups ketone (C = O), separated by a system of conjugated double bonds. Recent research efforts have concentrated on improved methods of manufacture and more economical finishing of traditional vat dyestuffs.[12,13,14] The vat dyestuff used in this paper were the C.I. Vat Yellow 33, C.I. Vat Blue 6, C.I. Vat Blue 18, C.I. Vat Green 1 and the C.I. Vat Green 3, all of them of high alkalinity, classified as IN process, with temperature of maximum affinity at 60 ºC, applied by semi-pigmentation process according to the manufacturer's instructions (Dystar).

2. Experimental

2.1. Laboratory Equipments

Gehaka AG 200 Analytical Balance, Konica Minolta CM-3600d Spectrophotometer, Nova Ética Jar-test 218 BDL, Mathis HT Alt-1, Perspirometer, Photochemical batch reactor with two 6W UV-C lamps and magnetical stirrer. Processing Machinery: HT Riviera Eco Metalwork with capacity of 50 kg and instaled potency of 7.4 kWh; Etna GHV-2000 steam generator with production capacity of $5.56 \cdot 10^{-1}$ kg·s^{-1}, maximum allowable operating pressure (MAOP) equal to 1.0 MPa operating with 85% of efficiency. Those equipments were used to calculate the energy balances and ecological cost.

2.2. Reagents

Solution of aluminum sulphate 10% and acrylic non-ionic polymer 5ppm supplied by Damarfe-Brazil; sodium chloride, sodium carbonate, hydrogen peroxide 35%, sulfuric acid 98%, sodium hydroxide 50ºBé, sodium silicate 95% and sodium dithionite 90% supplied by Cromoline - Brazil; non-ionic wetting agent, non-ionic detergent, anionic levelling agent, catalase enzyme, C.I. Reactive Yellow 145, C.I. Reactive Red 195, C.I. Reactive Blue 19, C.I. Reactive Blue 21 and C.I. Reactive Black 5 supplied by Golden Quimica - Brazil; C.I. Vat Yellow 33, C.I. Vat Blue 6, C.I. Vat Blue 18, C.I. Vat Green 1 e C.I. Vat Green 3 supplied by Dystar - Brazil.

2.3. Other materials

Cotton knit, 30/1 Ne carded yarn, LFA 7.5 and gramature of 120 g·m^{-2}, produced in an Orizio circular monofronture machine, John/C model, 3.0 feeders·inch^{-1}, diameter of 30 inch, 28 gauge, 30 RPM.

2.4. Procedures

The dyeing processes were carried out using a 10:1 liquor ratio. The recipes of dyeing with reactive dyestuff are described in the Table 1 and the complete process is shown graphically in the Figure 1. The dyeings were executed under the instructions of the Golden Química, the company that supplied the reactive dyestuff used in this study.

***Table 1**. Recipes of dyeings with reactive dyestuffs*

	Dyestuffs and auxiliaries	Yellow 120643	Blue 194035	Green 186024
A	Non-ionic wetting agent ($g \cdot L^{-1}$)	0.50	0.50	0.50
	Non-ionic detergent ($g \cdot L^{-1}$)	1.00	1.00	1.00
	Levelling agent ($g \cdot L^{-1}$)	1.00	1.00	1.00
	Sodium hydroxide 50 ºBé ($mL \cdot L^{-1}$)	2.00	2.00	2.00
	Sodium silicate ($g \cdot L^{-1}$)	0.50	0.50	0.50
	Hydrogen peroxide 35 % ($mL \cdot L^{-1}$)	2.00	2.00	2.00
B	Sulfuric acid 98 % ($mL \cdot L^{-1}$)	0.14	0.14	0.14
C	Catalase enzyme (%)	0.50	0.50	0.50
D	Sodium chloride ($g \cdot L^{-1}$)	30.00	60.00	60.00
E	C.I. Reactive Yellow 145 (%)	1.00	-	1.10
	C.I. Reactive Red 195 (%)	-	0.48	-
	C.I. Reactive Blue 19 (%)	-	1.10	0.80
	C.I. Reactive Blue 21 (%)	-	-	1.50
	C.I. Reactive Black 5 (%)	-	1.7000	-
F	Sodium carbonate ($g \cdot L^{-1}$)	10.00	15.00	15.00
G	Levelling agent ($g \cdot L^{-1}$)	1.00	1.00	1.00

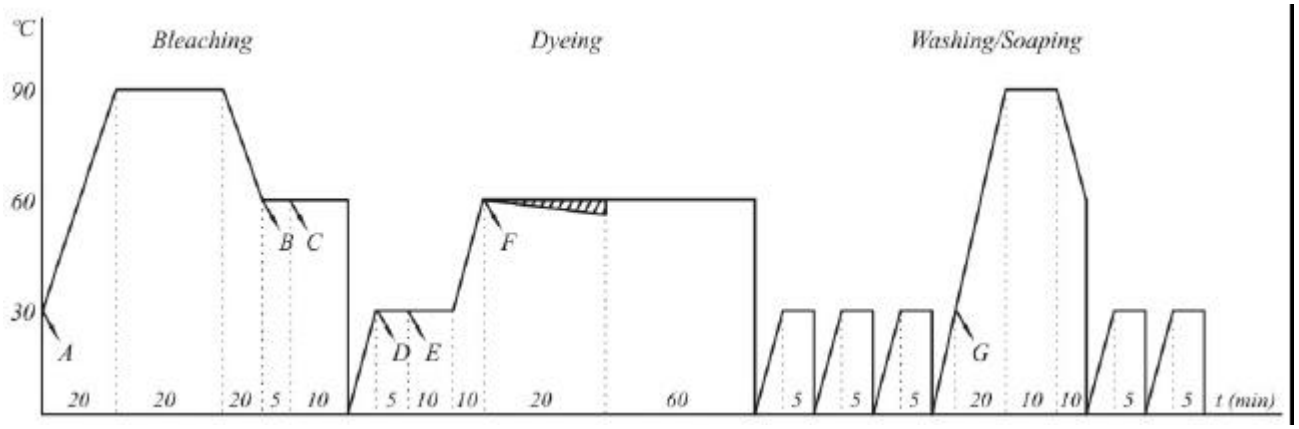

***Figure 1**. Procedure of the dyeing process with reactive dyestuffs*

The recipes of dyeing with vat dyestuff are described in the Table 2 and the complete process is shown graphically in the Figure 2. The dyeings were executed by the semi-pigmentation process proposed by Dystar, the company that supplied the vat dyestuff used in this study. All baths from all dyeings were collected and stored for the tests of effluents treatment.

***Table2**. Recipes of dyeings with vat dyestuffs*

	Dyestuffs and auxiliaries	Yellow 120643	Blue 194035	Green 186024
A	Non-ionic Wetting Agent ($g \cdot L^{-1}$)	0.50	0.50	0.50
	Sodium Hydroxide 50 ºBé ($mL \cdot L^{-1}$)	8.00	15.00	12.00
B	C.I. Vat Yellow 33 (%)	0.90	-	0.66
	C.I. Vat Blue 6 (%)	-	1.40	-
	C.I. Vat Blue 18 (%)	-	1.50	-
	C.I. Vat Green 1 (%)	-	-	0.66
	C.I. Vat Green 3 (%)	-	0.55	0.66
C	Sodium Dithionite ($g \cdot L^{-1}$)	4.00	8.00	6.00
D	Non-ionic Detergent ($g \cdot L^{-1}$)	1.00	1.00	1.00
	Levelling agent ($g \cdot L^{-1}$)	1.00	1.00	1.00
	Sodium Carbonate ($g \cdot L^{-1}$)	0.50	0.50	0.50
	Sodium Metasilicate ($g \cdot L^{-1}$)	0.50	0.50	0.50
	Hydrogen Peroxide 35 % ($mL \cdot L^{-1}$)	2.00	2.00	2.00
E	Sulfuric Acid 98 % ($mL \cdot L^{-1}$)	0.14	0.14	0.14
F	Catalase Enzyme (%)	0.50	0.50	0.50

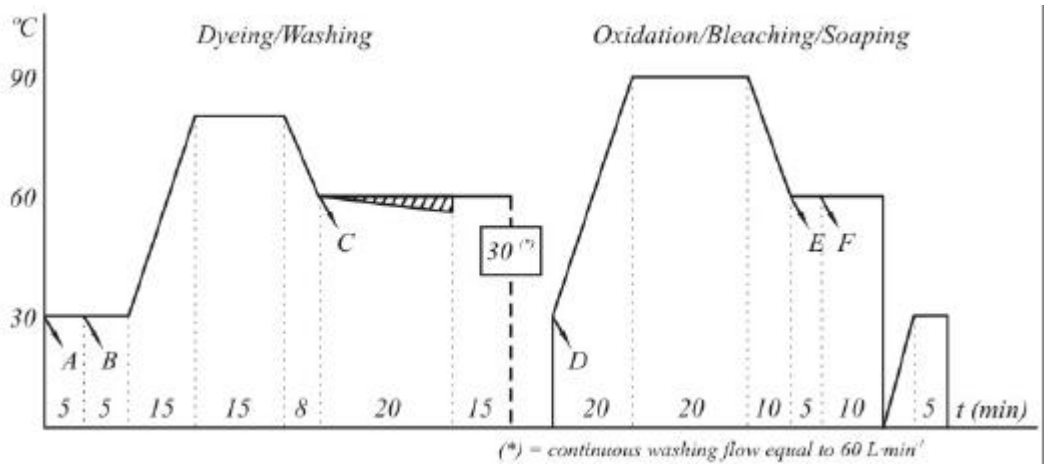

***Figure 2**. Procedure of the dyeing process with vat dyestuffs*

The Reflectance (%R) was determined by spectrophotometry under illuminant D65 and in the wavelength of maximum reflection of the colors. The treatment of the effluents was made in two principal steps, as illustrated in the Figure 3 and described below.

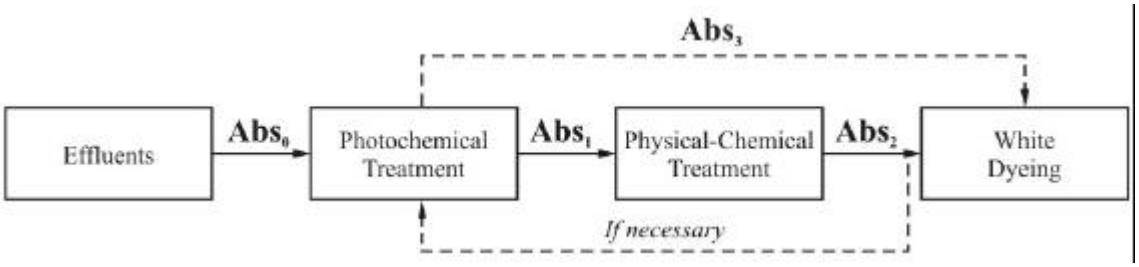

***Figure 3**. Blocks diagram representing the treatment of effluents*

Photochemical Treatment: oxidative processes advanced are characterized by the production of hydroxyl radicals that are highly reactive and show selectivity of attack with capacity to oxidize several organic compounds with a potential reduction of E_0 = 2.8 V.[15,16,17] All experiments were carried out in a photochemical batch reactor, with capacity of 1000 mL. The temperature was monitored using a thermometer and kept constant at 296 K, with constantly magnetic stirring. All samples were diluted five times and the UV irradiation was provided by two lamps (Phillips UV-C TUV 6 W) emitting a wavelength of 253.7 nm. Adding $2.27 \cdot 10^{-2}$ mol·L^{-1} of H_2O_2 and adjusting the pH value to 7.0, the samples were kept at those conditions for one hour.[18] The visible spectra during the degradation of dyestuff were recorded between 400 and 700 nm by spectrophotometry. The visible color removal was measured in the wavelength of maximum absorption. The aliquots were analyzed in acrylic buckets with 1.0 cm of optical path. The data were used to calculate the decolorization efficiency (D_{Ef}).

Physical-chemical treatment: after the photochemical step, the samples were submitted to same conditions of College of Technology SENAI Antoine Skaf effluent treatment plan. The parameters and the amount of chemicals used in Jar-Test were 20 RPM of mixing speed, 20 min of flocculation time and 20 min of sedimentation time, using 1.5 mL.L^{-1} of aluminum sulphate 10% and 1.0 mL.L^{-1} of 5 ppm polymer solution. The visible spectra after the treatment of dyestuff were recorded by spectrophotometry. The visible color was measured in the wavelength of maximum absorption. The aliquots were analyzed in acrylic buckets with 1.0 cm of optical path.

In order to verify the effectiveness of the treatment were made three dyeing of white, being one with the treated effluent of reactive dyeing, one with the treated effluent of vat dyeing and one with demineralized water. The recipe and the process of the white dyeing are described in Rosa et al.[19] and the results were compared by spectrophotometry under illuminant D65, CIELAB system.

For the calculation of the efficiency of discoloration (D_{Ef}) in the complete treatment of effluent was used the Equation 1:

$$\%D_{Ef} = \left[1 - \left(\frac{Abs_f}{Abs_o}\right)\right] \cdot 100 \quad (1)$$

where: D_{Ef} = decolorization eficiency; Abs_o = initial absorbance and Abs_f = final absorbance

HT Riviera Eco metalwork: the theoretical consumption of electric energy for each kilogram of substrate processed was determined by the time of process, applying the Equation 2.

$$Q_1 = \frac{t \cdot kWh \cdot 1000 \cdot 60}{50} = t \cdot kWh \cdot 1200 \quad (2)$$

where: Q_1 = J·kg^{-1}; t = minutes and kWh = instaled potency

For the amount of calorific energy required for each kilogram of substrate processed, was applied the Equation 3.

$$Q_2 = \Delta T \cdot Cp_{H_2O} \cdot m_{H_2O} \cdot 10^{-3} \quad (3)$$

where: Q_2 = J·kg^{-1}; T = Kelvin; Cp = J·kg^{-1}·K^{-1} and m = grams, adopting specific mass of water equal to 1.0 g·cm^{-3} and liquor ratio = 10:1

Steam Generator Etna GHV-2000: according to the supplier of fuel gas, the Gas Company of São Paulo (Comgas), the fuel gas is a gas mixing and has 89.0 % of methane, 6.0 % of ethane and 1.8 % propane. Based on the Inferior Calorific Power (ICP) standards laid down by ASTM D 3588-98 as being $3.70 \cdot 10^7$ J·m^{-3} for methane, $7.00 \cdot 10^7$ J·m^{-3} to the ethane and $9.23 \cdot 10^7$ J·m^{-3} of propane, the ICP calculated for the gas mixing was $4.02 \cdot 10^7$ J·m^{-3}.[20] In order to calculate the volume of gas needed for heating the amount of water used for dyeing a kilogram of substrate, was used the Equation 4, as described below.

$$V_1 = \frac{Q_2}{4.0 \cdot 10^7 \cdot E} \quad (4)$$

where: V_1 = $m^3 \cdot kg^{-1}$; Q_2 = $J \cdot kg^{-1}$ e E_{SG} = efficiency of steam generator

Calculation of the emission of CO_2: To calculate CO_2 emissions during the supply of heat energy, adopting that the gas is ideal and it is in normal conditions of pressure and temperature, was used the Equation 5.

$$mCO_2 = \frac{P \cdot V_1 \cdot 4.4 \cdot 10^{-2} \cdot CF}{R \cdot T} \quad (5)$$

where: mCO_2 = kg; P = 101.3 kPa; V_1 = m^3; R = 8314 $m^3 \cdot kPa \cdot mol^{-1} \cdot K^{-1}$; T = 273.15 K e CF = Factor carbon in the gas mixing equal to 1.10

3. Results and discussion

Dyeings: the results of dyeing processes are described in Table 3, by the values of reflectance (%R), the partial deviations (DL*, Da* and Db*) and the total deviations (DE). The total deviation between the colors did not exceeded 2.0, and those data are acceptable when compared with the standards used in the Brazilian industry of clothing.

***Table3**. Results of dyeings according CIELab system*

Pantone / Color	Data	Reactive	Vat	Partial Deviation	Total Deviation
120643/Yellow at 560 nm	%R	76.72	75.94	0.78	-
	L	86.88	85.43	1.45	
	a	-4.73	-4.67	-0.06	DE = 1.92
	b	65.56	64.3	1.26	
194035/Blue at 440 nm	%R	7.81	6.97	0.84	-
	L	31.3	32.61	-1.31	
	a	-2.54	-2.61	0.07	DE = 1.31
	b	-20.56	-20.48	-0.08	
186024/Green at 530 nm	%R	13.38	14.2	27.58	-
	L	43.5	44.08	-0.58	
	a	-24.92	-24.34	-0.58	DE = 0.83
	b	10.11	9.95	0.16	

*Obs: **%R** = reflectance; **L**, **a** and **b** = axis values from CIELab system; DE = total deviation*

In Table 4 are described the results of all stages of treatment of effluents. The experiments were undertaken to study just total decolorization for later reuse of water in new dyeings. The values such as salinity, chemical and biological oxygen demand or total organic carbon were not assessed, even because the intention was not discharge the effluent. According to Rosa, Tambourgi and Santana (2012), these values did not interfere negatively in five dyeing performed consecutively after the photochemical treatment of its effluent.

***Table 4**. Results of effluent treatment: **Abs_0** = absorbances of effluent without treatment; **Abs_1** = absorbances after first photochemical treatment; **Abs_2** = absorbances after physical-chemical treatment; **Abs_3** = absorbances after second photochemical treatment (if necessary) and **$\%D_{Ef}$** = decolorization efficiency*

Pantone / Color	Dyestuff	Abs_0	Abs_1	Abs_2	Abs_3	Abs_{Final}	% D_{Ef}
120643/Yellow	Reactive	0.1244	0.0135	0.0082	-	0.0082	93.41
	Vat	0.0377	0.0246	0.0002	-	0.0002	99.47
194035/Blue	Reactive	0.2518	0.0157	0.0094	-	0.0094	96.27
	Vat	0.3517	0.3449	0.0001	-	0.0001	99.97
186024/Green	Reactive	0.3492	0.1317	0.0332	0.0084	0.0084	97.59
	Vat	0.0360	0.0321	0.0001	-	0.0001	99.72

The bests values of decolorization were presented in the treatment of vat dyeings effluent, which had values close to zero with decolorization efficiency (D_{Ef}) above 99% in all cases. In addition, the effluent of the color Green 186024 made with reactive dyestuff had to be treated twice in photochemical step, in order to obtain a better result of decolorization. After the complete treatment, the effluents were used to make a white dyeing, comparing to a same one made with demineralized water. Both dyeings made with treated effluent had total deviation (DE) values lower than 2.0 when compared with the dyeing done with demineralized water. However, the treated vat effluent obtained nearest Luminosity (DL*) value than the treated reactive effluent. All values are described in the Table 5.

***Table 5**. White dyeings results*

White dyeing made with:	DL
Water (Standard)	0.00
Treated effluent – Vat Dyestuffs	**-0.52**
Treated effluent – Reactive Dyestuffs	-1.19

*Obs: **DL** = luminosity axis deviation*

Ecological Costs: the dyeings with vat dyestuffs also had lower values of ecological costs than the dyeings with reactive dyestuffs. The consumption of calorific and electrical energy of the vat dyeings were $5.08 \cdot 10^5$ joules lower than the reactive dyeings. The consumption of the fuel gas was also lower in $3.55 \cdot 10^{-3}$ cubic meter. As expected, the emission of carbon dioxide molecules was also lower in $7.80 \cdot 10^{21}$ molecules. The results are shown in Table 6.

***Table 6**. Ecological costs*

Dyestuff	Electricenergy (J)	Calorificenergy (J)	Gas fuel (m^3)	Emission of CO_2	
				Kg	Molecules
Reactive	$2.09 \cdot 10^6$	$6.27 \cdot 10^3$	$1.33 \cdot 10^{-2}$	$2.15 \cdot 10^{-2}$	$2.93 \cdot 10^{22}$
Vat	$1.58 \cdot 10^6$	$4.06 \cdot 10^3$	$9.77 \cdot 10^{-3}$	$1.57 \cdot 10^{-3}$	$2.15 \cdot 10^{22}$
Delta	$\mathbf{5.06 \cdot 10^5}$	$\mathbf{1.67 \cdot 10^3}$	$\mathbf{3.55 \cdot 10^{-3}}$	$\mathbf{5.72 \cdot 10^{-4}}$	$\mathbf{7.80 \cdot 10^{21}}$

4. Conclusion

It was demonstrated that the vat dyestuffs have certain advantages on the reactive ones. The dyeings presented smaller ecological costs values and have a great possibility of reutilization of their effluent. However, the dyeings made with kind of dyestuff need a little more attention than the dyeings with reactive dyestuff, mainly because of the greater number of variables in their processes. In addition, the final use of the fabric is also very important, as well as the customer's decision on which type of needed product. It is important to note that many studies must be made before dyeing any type of product. The variety of classes of dyestuff for the textile industry is immense and previous studies are extremely important to obtain the best results.

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