Recycling Of Coloured Broke for Manufacturing High Bright Paper

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ABSTRACT

With the expected growth in per capita consumption of paper 20 Kg by 2020 paper making raw material has become more of a concern to all pulp Paper and board mills. The current ratio of raw material for paper making is 40: 30: 20, wood: Agri-waste: waste paper respectively. Though recycled paper usage maximization is the order of the day, recycling of mill broke/ outside broke either white or coloured will be very much helpful not only for environmental aspect but also economic aspect. This paper discusses options for treating four types of coloured broke individually and also after blending. Treatment with ClO_2, Hypo, Sodium Hydrosulfite, H_2O_2 have been discussed and the best suitable approach for handling colored broke for high bright paper manufacture has been suggested.

Introduction

Utilisation of colored broke during same color paper manufacture is the most convenient approach to manage colored broke. But this is not practicable always, because of the associated operations such as rewinding, finishing, which naturally take more time after manufacturing is complete. So the storage of colored broke is inevitable. By frequent grade changes depending on order quantity, the generation of colored broke will increase and the excess broke needs proper treatment before further usage.

Colour stripping using oxidants and reducing agents are available techniques to bleach coloured broke. Oxygen with the combination of Hydrogen peroxide or Ozone is an effective approach for coloured broke bleaching (1, 2) .Oxone , a Triple salt of potassium peroxy mono, peroxy di and persulfate is also known for coloured broke bleaching (3).FAS (Formamidine Sulfinic acid)gives good result as compared to Sodium Hydro sulfite (4,5,6). A major difficulty in recycling these grades of paper is the problems associated with decolorizing the dyes present in the paper.(7)

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Literature Review

First, wastepaper recycling and problems due to color from dyed papers will be discussed. Next, the basics of color and dye chemistry will be examined.. Finally, decolorization of dyes oxidants and reductants are dicussed

Selection of appropriate Recycling Technology

A great deal of effort is required for designing the process conditions and operations for bleaching of coloured broke based upon the final brightness.The colour of broke determines the treatment . The main problem is associated with the handling and storage of broke. The storage place should be free from contaminants.

Dye Removal Processes

Removing colored dyes from wastepaper consists of two processes. Color stripping allows dyes to be washed away. Most paper dyes have a high tinctorial strength (high molar absorptivity). Removal by simple dilution and washing would require an excessive amount of water. Bleaching and decolorization both refer to the destruction of light-absorption capacity.

1. Color stripping - release of attached colored material from the fibers into the solution.
2. Bleaching or decolorization - destruction of the dye's ability to absorb visible light.

Theory of Color:

Generally, basic dyes are used for mechanical and unbleached pulp. Acid, cationic, and direct dyes are used for bleached chemical pulps. Chromaticity is defined by CIE LAB is 'a*' (green-Red) and ' b*' (Blue yellow)values .For a chromactic paper brightness is purely depends on the function of ' L*' (Lightness/ whiteness) value.

In this paper, the suitability of pulp for manufacturing Hi brite paper is verified by the standard given by TAAPI T 524 om-94 (11), which defines the white paper near white paper have $L \geq 84.0$ and a chromaticity value $\sqrt{(a2+b2)} \leq 10.0$. Colour index (CI) Shows the changes in colour, it is calculated by the given formula

$$\Delta E = \sqrt{\Delta L2 + \Delta a2 + \Delta b2} \quad - \quad (12)$$

Sharp and Lowe (13) and Rangamannar (14) used the ΔE value to evaluate the efficiency of colour stripping process

1.8 Dye Chemistry

The possibility of organic compounds to absorb light and produce color is created by the overlap of π-orbitals. Dye chromogens consist of electron-donor(s) and electronacceptor(s) interacting through a conjugated

Current Bleaching Methods In Wastepaper Recycling

Oxidizing Agents

D	Chlorine dioxide
H	Sodium hypochlorite
O	Oxygen bleaching
P	Hydrogen peroxide
Z	Ozone bleaching

Reducing Agent

FAS	Formamidine sulfinic acid (Thio urea dioxide)
Y	Sodium hydrosulfite (dithionite)

Table below provides the Oxidation Potentials of Bleaching Agents as per Bierman and Kronis

Species	Structure	Standard Oxidation potential mV	Potential Relative to Cl2 (1.00)
Chlorine dioxide	ClO_2	1.57	1.15
Chlorine	Cl_2	1.36	1.00
Hypochlorite	ClO-	0.89	0.65
Hydrogen peroxide	H_2O_2	0.88	0.65
Hydrosulfite	S_2O_4-	1.12	

Reactions of Bleaching Agents as per Bierman and Kronis 15

Oxidizing Agents

Chlorine $Cl_2 + 2e- \rightarrow 2Cl-$ Eo = 1.36 V

Chlorine Dioxide $ClO_2 + 4H+ + 5e- \rightarrow Cl- + 2H_2O$ Eo = 1.57 V

pH 4 b c Eo = 1.38 V

Hydrogen peroxide

(acidic) b $H_2O_2 + 2H+ + 2e- \rightarrow 2H_2O$ Eo = 1.78 V

(basic) $H_2O_2 + 2e- \rightarrow 2OH^-$ Eo = 0.88 V

Reducing Agents

Hydrosulfite (Dithionite) $2SO_3 + 2H_2O + 2e- \rightarrow S_2O_4- + 4OH-$ Eo = -1.12 V

pH 5-6b → Eo = -0.88 V

Formamidine Sulfinic Acid (FAS or thiourea dioxide)

$H_2CONH_2 + H_2O + HSO_3$ - + 2e- → $NH_2C(=NH)SO_2H$ + 3 OHAt

pH 10, 20°C, vs. Pt//Ag/AgCl, v = -0.80

Eo is standard reduction potential relative to hydrogen

double bond system

1.9 Electronic Requirements For Color

Dyes are organic compounds. Like all organic compounds, their atomic orbitals combine to form molecular orbitals. When a group with π orbitals (e.g. NO_2 or COOH) is attached to an aromatic compound, overlapping of the two π orbitals normally occurs, leading to new bonding and antibonding states. Orbital overlapping and combination also occurs when aromatic carbons carry substituents that have lone pair of electrons (e.g. OH, NR_2, etc.) Formation of hydrogen-π bonds has been suggested as a source of dye-fiber attraction. The degree of conjugation (number of π orbitals and electrons) determines whether the electromagnetic radiation absorbed is within the range of visible wavelengths.

Chromophore:

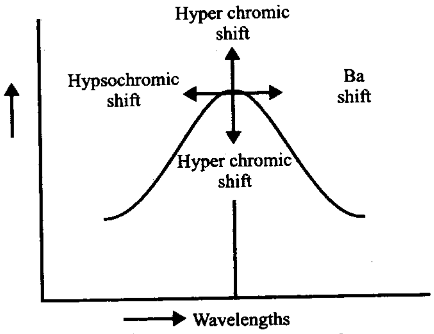
it is the functional groups which are unsaturated and they cause a compound to become coloured. Examples of chromophores are N=N-, -C=C-, -C=N- and -C=O.

Auxochrome

- Auxochromes are groups that does not impart color to the compound but increase the color of the compound. Functional groups such as hydroxyl (OH), amino ($-NH_2$), nitro ($-NO_2$), alkyl (-R), OH, OR, NH_2, NHR, NR_2, SH are common examples for auxochrome. The effect of the auxochrome is due to its ability to extend the conjugation of a chromophore by the sharing of non-bonding electrons.

Experimental Methods

The bleaching of coloured broke was carried out according to the following conditions. Colored Broke samples were collected from the mill and the

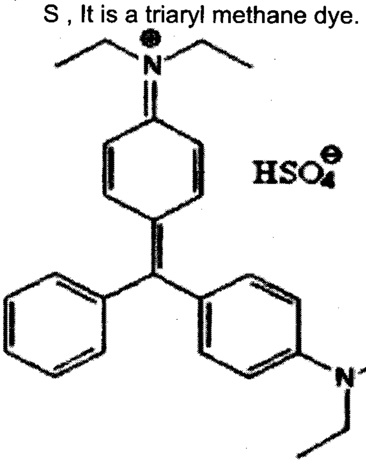


Approaches to Decolorize Dyes or Color-Strip Dyed Fibers

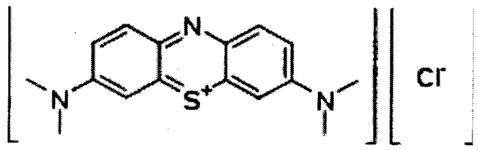
Component	Examples	Approaches for Decolorization/Color-Strip
Electron-donating group (Auxochrome)	$-NH_2$, -NHR, $-NR_2$ -OH -OR	Oxidize to lower electron density Split from molecule
Electron-accepting group (Chromophore)	-C=O -N=N- $-NO_2$ $-NR_{3}+$	Reduce to add electron density Split from molecule
Conjugated double bonds	-C=C- -N=N- -C=N	Double bonds by redox rxns Oxidize: C? C=O N? N=O Reduce: C? CH_2 N? NH_s Add to bond(s): convert ? bonds to ? bonds C=C ? ClC-CCl or C-Cepoxid
Solubilizing groups	$-SO_3Na$, -COONa $-N+H_2HCl-$, $-N+R_3Cl-$	Change pH to change solubility, fiber affinity
Reactive groups	Covalent bonds to fiber	Cleave dye-fiber bonds

Chemical Structure Of Dyes Used In Paper Making

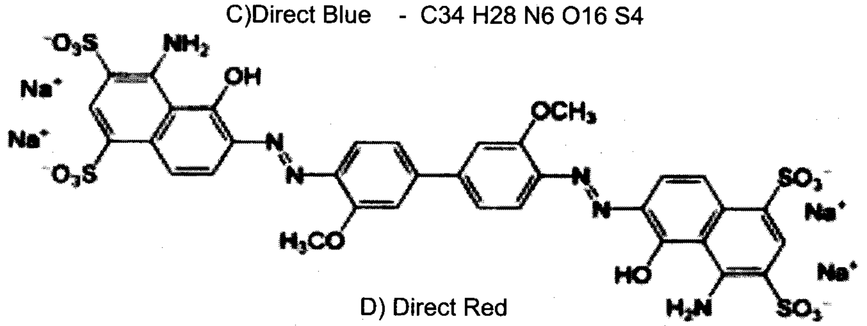
a) Brilliant Green - C27 H33 N2 HO4 S , It is a triaryl methane dye.



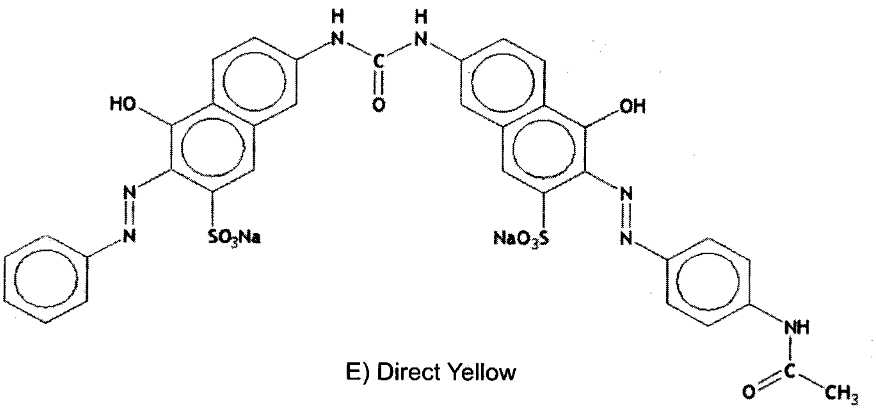
B) Methylene Blue - C16H18N3SCl



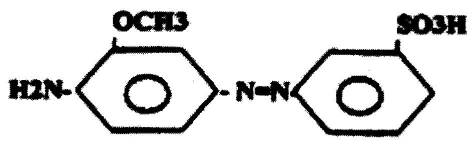
C)Direct Blue - C34 H28 N6 O16 S4



D) Direct Red



E) Direct Yellow



paper samples were soaked and disintegrated in standard disintegrator and then dewatered to uniform consistency in Buchner funnel under suction.

Dye bleaching experiments were carried out with 20g OD pulp in polythene bags with different oxidants such as chlorine di oxide, hydrogen peroxide, and hypochlorite under varying dosages. Reductive bleaching was carried out with hydrosulfite. The bleaching conditions maintained are given along with the result.

After bleaching the pulp samples were washed and thickened and brightness pads were made for measurement of color values in terms of L* a* and b*.

2.1 Materials And Reaction Equipment

Bleaching experiments were carried out under standard conditions in polythene bags. The pulp samples after addition of required bleach chemicals and mixing were checked for pH and then kept in thermostatic water bath at required temperature for the desired duration. The samples were kneaded periodically during the bleaching time. At the end of bleaching, final pH was measured and the pulp was washed over Buchener funnel with DM water with recirculation of fines. Standard brightness pads were made at Buchner funnel over filter paper with pulp equivalent to 3 g OD. The pads were pressed under standard sheet press between standard blotters and then air dried before measuring the optical properties.

The optical properties such as Brightness, L*,a* and b* were measured in Technidyne brightness tester as per Tappi standard and Color index was computed from the values as mentioned before.

2.2 Results and discussion

Colored papers are manufactured as per the shade requirements from the customer and depending on the type of shade sample received from customer, different dyes are used to achieve the desired shade. Table 1 shows the dyes used for manufacturing different colored papers.

The colored paper broke is generated till required shade is achieved and during post production operations such as winding, rewinding and trimming. Usage the broke in the same shade paper manufacture is the most convenient way of handling. However that is not always practicable since the

Table 1 Dyes used for colored papers

Sl.NO	Colour of the sample	Name of the dye used
1	Color printing(green)	Brilliant green
2	Color printing (Blue)	Direct Blue & Methylene Blue
3	Color printing (pink)	Direct Red
4	Color printing (yellow)	Direct yellow & Direct green (tint matching)

broke has to be stored till next order. This poses lot of difficulties and warrants lot of storage space. Hence it is pertinent to consume the colored broke. But before doing so it has to be decolorized for use in regular white grades.

The color removal or color stripping process is an important process for suitability of colored broke to be used in white grades. The color removal is accomplished with oxidants or reducing agents as described earlier. But a comprehensive approach to handle different colored broke needs to be devised since different colors have different bleaching response and thus needs a calculated approach to handle pink. Blue, green and yellow broke.

Compared to virgin bleached pulps, the colored pulps have L*, a* and b* values, which are called the color coordinates, as given in table 2.

The L* value gives the Lightness representing how white the pulp is 100 represents pure white and 0 represents pure black. a* value when negative is green and when positive is red. Like wise b* value when negative is blue and yellow when positive. The chromaticity indicates the intensity of the color.

As evident from the table, addition of dye for coloring results in reduction in L* value. So while bleaching or decolorizing the colored broke for usage along with virgin pulp for high bright paper, the L* value has to be improved to acceptable levels in addition to removing the dye which is indicated by a* and b* values.

Color stripping experiments were carried out with different colored broke pulp individually with different oxidants and also with Hydrosulfite reducing agent, and the response of different colors to different bleaching agents were studied.

The next step is colour stripping experiments was carried at a given conditions. Tables 3,4,5 and 6 presented below give the effect of different ClO_2 dosage on color stripping of green broke.

Constant conditions for chlorine di oxide color stripping

20 gm OD pulp
60-65 c
1.30 hrS
12 % CY
3.5 pH

As seen from the tables, a dosage of 2.0% Chlorine di oxide is able to decolorize green and blue dye and the pink dye gets decolorized at 1.5% dosage. But the yellow dye is quite resistant even at dosage levels of 2.0% chlorine di oxide. So it may be inferred from the above that the colored broke of green blue and pink can be comfortably mixed with the extraction stage of chlorine di oxide bleaching sequence and the final single stage chlorine di oxide is sufficient to decolorize the colored broke to a level of about 80% brightness.

Table 2 Color coordinates of Colored papers in comparison to virgin pulps

Name of the sample	L* Value	a* value	b* value	Yellowness Index	Brightness % ISO	Chromaticity √(a*2+b 2)
Green	84.96	-18.57	-4.13	-24.49	71.97	19.02
Blue	82.35	-6.49	-12.68	-33.90	72.62	11.89
Pink	77.76	32.95	-3.12	25.76	55.66	33.09
Yellow	90.56	-9.7	49.97	69.07	29.82	50.90
Bleached wood pulp	96.32	-0.62	3.26	5.73	86.48	3.32
Bleached bagasse pulp	95.32	-0.72	3.10	6.01	86.51	3.18

Table 3 : Color stripping of Green broke using Chlorine di Oxide

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√(a*2+b 2)
Green	84.96	-18.57	-4.13	71.97	-24.49	19.02
0.5% ClO2	88.12	-9.23	-1.32	73.56	-10.22	9.32
1.0% ClO2	92.12	-1.88	4.45	76.60	7.21	4.03
1.5% ClO2	94.22	1.26	5.23	78.60	8.01	5.37
2.0% ClO2	94.92	2.44	6.23	79.05	8.26	6.69

Table 4: Color stripping of Blue broke using Chlorine di Oxide

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√a*2+b 2)
Blue	82.35	-6.49	-12.68	72.62	-33.9	11.89
0.5% ClO2	85.12	-4.65	-2.65	73.35	-1.26	5.35
1.0% ClO2	90.46	-2.00	5.32	73.85	8.94	5.68
1.5% ClO2	91.26	1.21	7.25	76.25	9.65	7.35
2.0% ClO2	92.86	1.71	6.29	78.25	8.65	6.56

Table 5: Color stripping of Pink broke using Chlorine di Oxide

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√(a*2+b 2)
Pink	77.76	32.95	-3.12	55.66	25.76	33.09
0.5% ClO2	85.26	10.65	1.26	68.24	14.25	10.70
1.0% ClO2	93.03	-0.39	6.40	75.04	12.04	6.41
1.5% ClO2	94.01	2.60	7.25	79.25	6.25	7.70
2.0% ClO2	95.83	3.01.	8.01	83.24	3.26	8.56

Table 6: Color stripping of Yellow broke using Chlorine di Oxide

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√(a*2+b 2)
Yellow	90.56	-9.7	49.97	29.82	69.07	50.90
0.5% ClO2	90.62	-3.26	42.38	34.26	61.25	42.50
1.0% ClO2	90.73	-5.73	38.92	37.68	59.34	39.34
1.5% ClO2	91.00	-1.25	32.65	32.25	50.23	32.67
2.0% ClO2	92.44	1.24	30.98	31.25	39.26	31.00

Colour stripping with H_2O_2

Similar experiments were carried out with different dosages of peroxide and the results are presented in tables 7,8,9 and 10 below.

Constant bleaching conditions for peroxide treatment

20 gm OD pulp
80-85 c
1.00 hrS
12 % CY
10.5 10.8 pH

As may be seen from the results, peroxide also does not have the capacity to decolorize yellow broke and compared to chlorine di oxide, it has a lower decolorizing efficiency for pink colored broke. In case of blue broke, dosage beyond 1.5% produces yellowing resulting in lower brightness.

Color stripping using Hypochlorite as Oxidant

Hypochlorite being a cheaper option as an oxidant, the efficiency of the same in color removal from colored broke was studied. Like other two experiments conducted, the hypochlorite color removal was also performed under different dosage levels and the results presented below in Tables 11, 12, 13 and 14 shows the outcome of the studies.

Colour stripping with Hypochlorite was performed under following constant conditions

20 g OD pulp
60-70 deg C
1.00 hr
12 % CY
11.0 pH

As may be seen from the results, the effect of Hypochlorite for color stripping is found to be effective for green and blue colored paper and the target brightness of 78-80% ISO is obtained with 2% dosage. However with pink colored broke the effect was lower and inferior to the performance of chlorine di oxide. With hypochlorite also the color stripping of yellow broke was poor.

Color stripping with Sodium hydrosulphite

Reductive bleaching is a preferred step in bleaching of deinked pulp, which is usually incorporated for color stripping

Table 7 : Color stripping of Green broke using Hydrogen Peroxide

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b 2)
Green	84.96	-18.57	-4.13	71.97	-24.49	19.02
0.5% H2O2	86.12	-17.25	-4.00	72.64	-21.40	17.70
1.0% H2O2	88.23	-8.25	1.02	76.54	-10.22	8.31
1.5% H2O2	90.25	-1.06	5.65	79.65	3.68	5.78
2.0% H2O2	91.25	2.26	6.01	80.64	4.35	6.42

Table 8: Color stripping of Blue broke using Hydrogen Peroxide

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b* 2)
Blue	82.35	-6.49	-12.68	72.62	-33.9	11.89
0.5% H2O2	84.65	-1.25	-6.75	73.75	-7.26	6.86
1.0% H2O2	85.32	2.02	-1.0	76.9	-2.26	2.25
1.5% H2O2	87.36	4.26	5.25	78.25	4.26	6.76
2.0% H2O2	90.36	6.01	6.81	72.65	11.26	9.08

Table 9: Color stripping of Pink broke using Hydrogen Peroxide

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b 2)
Pink	77.76	32.95	-3.12	55.66	25.76	33.09
0.5% H2O2	80.25	30.26	-1.09.	50.23	20.6	30.28
1.0% H2O2	87.28	22.16	4.26	62.59	18.25	22.56
1.5% H2O2	90.26	10.26	5.03	68.97	12.65	11.43
2.0% H2O2	91.26	6.25	6.06	72.36	10.36	8.70

Table 10: Color stripping of Yellow broke using Hydrogen Peroxide

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b 2)
Yellow	90.56	-9.7	49.97	29.82	69.07	50.90
0.5% H2O2	90.62	-8.26	44.65	27.65	66.58	45.40
1.0% H2O2	91.00	-1.02	20.65	38.98	59.36	44.11
1.5% H2O2	93.00	2.0	16.25	44.56	50.36	16.37
2.0% H2O2	93.81	3.21	14.26	50.56	39.58	14.62

Table 11 : Color stripping of Green broke using Hypochlorite

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b 2)
Green	84.96	-18.57	-4.13	71.97	-24.49	19.02
0.5% Hypo	88.26	-12.35	-1.03	75.63	-10.26	12.39
1.0% Hypo	91.23	-5.33	1.86	77.03	-0.53	5.65
1.5% Hypo	92.23	-1.23	2.03	78.26	2.01	2.37
2.0% Hypo	92.93	2.26	4.26	79.26	3.68	4.82

Table 12: Color stripping of Blue broke using Hypochlorite

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b* 2)
Blue	82.35	-6.49	-12.68	72.62	-33.9	14.24
0.5% Hypo	84.26	-4.56	-6.36	74.26	-8.01	7.83
1.0% Hypo	86.16	-3.55	-3.12	75.36	-8.77	4.73
1.5% Hypo	88.16	-1.06	-2.29	76.36	-6.85	2.52
2.0% Hypo	89.65	2.36	3.65	78.65	-2.35	4.35

Table 13: Color stripping of Pink broke using Hypochlorite

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b 2)
Pink	77.76	32.95	-3.12	55.66	25.76	33.09
0.5% Hypo	84.26	21.36	1.06	65.35	18.25	21.39
1.0% Hypo	89.05	9.41	2.06	71.78	12.25	9.63
1.5% Hypo	92.32	6.28	3.64	73.65	10.25	7.26
2.0% Hypo	93..84	7.26	5.26	74.26	9.28	8.97

Table 14: Color stripping of Yellow broke using Hypochlorite

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b 2)
Yellow	90.56	-9.7	49.97	29.82	69.07	50.90
0.5% Hypo	90.90	-7.84	40.29	32.26	60.34	41.05
1.0% Hypo	90.90	-6.81	37.87	39.29	56.92	38.47
1.5% Hypo	91.06	-1.28	30.26	45.65	55.36	30.29
2.0% Hypo	91.66	2.26	28.25	40.45	59.60	28.34

Table 15 : Color stripping of Green broke using Hydrosulfite

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b 2)
Green	84.96	-18.57	-4.13	71.97	-24.49	19.02
0.5% Hydros	88.65	-14.25	-1.36	72.98	-20.49	16.62
1.0% Hydros	89.26	-11.23	-0.32	73.26	-18.26	11.23
1.5% Hydros	90.23	-8.26	2.23	74.26	-12.03	8.56
2.0% Hydros	91.26	1.26	3.6	76.26	-9.81	3.81

Table 16: Color stripping of Blue broke using Hydrosulfite

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b* 2)
Blue	82.35	-6.49	-12.68	72.62	-33.9	14.24
0.5% Hydros	84.56	-4.26	-6.26	74.26	-6.25	7.57
1.0% Hydros	85.56	-1.26	-3.26	75.26	-3.26	3.49
1.5% Hydros	88.26	2.36	1.26	76.23	-1.26	2.68
2.0% Hydros	90.26	3.6	2.86	78.26	2.36	6.09

Table 17: Color stripping of Pink broke using Hydrosulfite

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b 2)
Pink	77.76	32.95	-3.12	55.66	25.76	33.09
0.5% Hydros	83.26	28.36	-1.01	60.25	28.68	28.38
1.0% Hydros	86.66	26.36	2.36	62.25	24.26	26.47
1.5% Hydros	88.36	24.36	3.26	64.26	21.23	24.58
2.0% Hydros	90.69	22.36	4.26	66.98	20.68	22.76

Table 18: Color stripping of Yellow broke using Hydrosulfite

Name of the sample	L* Value	a* value	b* value	Br% value	YI value	√ (a*2+b 2)
Yellow	90.56	-9.7	49.97	29.82	69.07	50.90
0.5% Hydros	90.86	-8.46	44.25	32.25	65.26	45.05
1.0% Hydros	90.33	-3.26	40.25	30.25	60.25	40.38
1.5% Hydros	91.05	-0.36	38.26	28.66.	62.26	38.26
2.0% Hydros	90.29	2.36	30.28	26.25	64.46	30.37

of dyes and colored printing inks. Hydrosulfite bleaching of colored broke was also performed and compared with oxidative color stripping process. The hydrosulfite bleaching of colored broke was performed under the following conditions

20 gm OD pulp
60-65 c
1.00 hrS
12 % CY
6.0 pH

The results of the hydrosulphite bleaching of various colored broke samples are presented in tables 15,16,17 and 18.

In the case of Hydrosulfite also the response of yellow broke towards decolorisation was poor. Green and blue broke responded better but final brightness obtained could be only 75% ISO. The Pink broke response was also not satisfactory towards hydrosulphite.

Reasons for Poor response of yellow color towards oxidants and reductants

Investigating the poor response of yellow color towards decolorisation using oxidants and reducing agents lead us to the following fact.

Direct Yellow is a symmetrical compound consisting of two, 4, 4'-dinitro, 2, 2'-disulfonated stilbene units that have been joined together by the conversion of a nitro group from each unit into an azo bond. No electron-donating auxochromes are in the molecule. This structure lacks phenolic groups and cannot form a hydrazone. The nitro groups in the *para* position are strong chromophores, as is the azo bond. In addition, the electron-withdrawing *para* nitro groups reduce the already low π electron density of the stilbene units. The low electron density results in low reactivity and explains why Direct Yellow does not react well with chlorine compounds, FAS, and hydrosulfite. The dye can be decolorized by ozone because ozone creates highly-reactive free radicals.

Plant trials :1

Among the various chemicals tried for decolorisation of broke for high bright pulp, chlorine di oxide showed the best performance while peroxide and hypochlorite followed Chlorine di oxide. The color stripping with reducing agent Hydrosulfite was found to be intermediate. Based on the above findings, chlorine di oxide bleaching trials were conducted with mixed broke of green, blue and pink. Results were compared with bleaching of mixed broke of green, blue, pink and yellow.

As may be seen, in this case also the introduction of yellow broke impaired the efficiency of decolorisation by Chlorine di Oxide and mixed broke without yellow gave satisfactory performance.

Table 19: Green + pink + blue blended broke bleached with ClO2

Dosage of ClO2	Br% value
0.5%	49.76
1.0%	56.25
1.5%	68.79
2.0%	74.26

Table 20 : Mixed Broke including Yellow broke bleached with ClO2

Dosage of ClO2	Br% value
0.5%	48.52
1.0%	52.36
1.5%	54.26
2.0%	55.36

Plant trials:2

The mixed broke was bleached in the regular ECF bleaching of bagasse pulp in the plant.Initial brightness of mixed broke 45 % (with yellow broke). The brightness at different stages of bleaching were as below

As seen, the introduction of yellow broke results in lower final stage brightness while mixing other colored

With yellow broke

ECF Stage	% Br
D0	62/64/63/66/65
EOP	70/68/70/71/72
D1	78/80/79/81/79

With out yellow broke the brightness at different stages were as below

ECF Stage	% Br
D0	68/69/70/71/67
EOP	78/76/79/79/78
D1	85/86/86//84/86

broke did not affect the bleaching performance.

Summary Of Results

From the above experiments and mill experience, the decolourisation of yellow broke is not possible by Chlorine di oxide.H_2O_2, Hypo, sodium hydrosulphite. Hence it is recommended to segregate yellow broke, while other broke such as green, blue and pink can be blended and bleached by a single stage Chlorine di oxide which is most effective. Hence blended broke can be handled by mixing it with extraction stage of ECF bleaching and subjecting it to final Chlorine di oxide stage is the most promising way to manage colored broke.

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