Shade Variation In Paper

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The shade variation in paper made on the machine as well as the working up of the stuff in the stock preparation alongwith the brightness of pulp received from the pulp mill have their impact to such an extent that there has to be a fundamental study to investigate the many different variables that contribute to the so called shade variation in the paper finished. This has a direct impact of the quality of paper.

The different variables that are considered contributing to this end can be listed as under alongwith the source where they are generated

	Variable	Source
1.	Pulp Brightness and Yellowness	Pulp Mill
2.	Reversion of colour	Stock Preparation and Bleaching conditions in Pulp Mill.
3.	Quality of process water	Contaminants in process water,
4.	Dyes	Quality of supply.
5.	Mode of addition of chemicals and colour fixing.	Stock Preparation.
6.	Change in shade of Paper on drying.	Paper machine as well as the sensitivity of dye to to heat.
7.	Human problem	All sources.

Each of the above variables had to be studied in detail to find a solution to the problem, considering the nature of problem at each stage, colouring the stock and the treatment the pulp had before it reaches the stock preparation.

The Pulp brightness has been considered steady to start with, and the reversion of colour has been studied separately. In this report, the quality of the dye, mode of addition, the characteristics of the dyes used by us, and the process water have been discussed in detail, with a view to assess the intensity of the variable in respect of its contribution to shade variation and to how to minimise its impact.

1.0 Stock Dyeing :

There are three different methods of dyeing paper, namely, Beater dyeing, Dip dyeing, and Surface staining. In the beater dyeing, the most extensively used process of dyeing stock, the dyestuff solution or dispersion is added to the stock before the web formation. However, in large mills, the dye is normally added either batchwise or continuously to the stock, in the mixing chest. The required additives are added to the stock to get the desired degree of sizing, colour, and filler loading. However, the operations are governed by the specific nature of the dyes and chemicals added to the stock in the mill, as well as the quality of paper desired to be produced. There are also many varieties of dyes available in the market. They can be broadly classified as acid, basic and direct dyes. Many of these dyes are water soluble. We have taken up the case of basic dye in colouring pulp as a specific case. We use many basic dyes for colouring our bleached pulps. A list of these dyes in use alongwith its chemical nature is listed hereunder :—

COMMON BASIC DYES

S. No.	Dye	Chemical nature
1.	Auromine	Diphenyl methane dye.
2.	Methyl violet	Triphenyl methane dye.
3.	Victoria Blue	Diphenyl Naphthyl methane dye.
4.	Rhodamine	Xanthane dye.
5	Methylene Blue	Thiazine Dye.

It is important that we consider both the nature of pulp and the characteristics of the dye in respect of the type of shade desired alongwith fastness of colour to various atmospheres, like water, light, heat, alkali and acid, before we use the dye for a particular end use.

There has to be an atmosphere created which is compatible to both dye, and the pulp to be coloured.

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The basic dyes are cationic in nature and have no affinity for lignin-free pulps. Most of the basic dyes are either chlorides or zinc chloride double salts of dye bases of various constituents listed above. The main features of the basic dyes are their outstanding brilliance, and high colour yield apart from the fact that there is practically no colour loss in the white water within the range of pH 4.5—5.0, their retention is very poor at the neutral pH. The colour fastness of these dyes is outstanding, though poor to light. The fastness is generally good to acids like acetic acid and alum solution and moderate to alkali. In view of the above advantages, the basic dyes are mostly used for colouring both bleached and unbleached stocks. However, the basic dyes do not fix on to bleached pulps, so that in papers in which no size or alum is used, the dyeing of unbleached pulp is better with basic dyes, while very poor when used with bleached stocks practically free of lignin.

These dyes can also be used for on-machine one stage staining or similar surface staining processes. One other property of the dyes is note-worthy here, namely, an acid and a basic dye should not be dissolved in the same vessel. Solution of these dyes must be added separately to the pulp. The first dye solution must be allowed to disprese evenly in the pulp before the second dye solution; the sequence is of no significance. (This point is studied experimentally and discussed elsewhere in this report). A fine precipitate is formed when the two dye solutions react with one another on their addition to the pulp. In many cases this precipitate is advantageous in dyeing, namely, less stained water and improved fastness of paper to drying on hot dryers, reduced twosidedness in dyeing heavily filled papers.

2.0 Whitening Agents :

Before we can go into the technology of dyeing papers under various conditions, it is essential that we understand the chemistry of optical whitening agents. They behave like direct dyes when added to paper. They are water soluble and get absorbed on to the paper without any fixing agent. The general practice is to dissolve them in warm water, dilute with cold water and add to the stock before the addition of sizing chemicals like alum.

Optical brightners or whitening agent when treated to paper grade pulp, depend for their action on their ability to absorb U.V. Light and remit them in the blue end of the visible spectrum of light, thereby imparting a bluish white tint to the paper that ultimately offsets the yellowness of the pulp.

Most comonly used Optical Whiteners in paper industry are fluorescent compounds which are mostly bis (1,3,5-Triozinyl) derivatives of 4,4-dimino stilbene disulfonic acid.

To derive maximum benefit of these optical brightners Harkavy(1) suggested the following :—

1. Replacing the part of alum with sulphuric acid in the alum blend for sizing since aluminium ions have dulling effect on the optical activity of the optical brightners added to the pulp.
2. Use of polyphosphates as sequestrants.
3. Use of iron free alum.

It is an established fact that hydrogen ion concentration or acidity of the medium during the addition of optical brightners play a vital role in enhancing the final whiteness of the pulp.

The table 1 compares the final whitness of the pulp to which an optical whitening agent was added under different ionic conditions. Many of the common whitening agents are not stable to the usual range of back water at a pH of 4.5-5, for, they lose their whitening effect and become dull. The best acidity values for optimising the effect of either whitening agent or the dye is added to the pulp, is 80-120 ppm as SO3 ion, in the back water of the machine.

TABLE–1

Comparison of Brightness and Yellowness in Pulp contributed by water (containing iron and other contaminants) and Sizing Chemicals.

Legend : P—Pulp : R—Rosin ; A—Alum : T—Talc : T—Tinopal.

Pulp used was imported bleached variety.

Conditions of addition :

Basis : 100 parts of pulp.

Rosion	1.2 %
Alum	4 %
Talc	20 %
Tinopal	0.2 %

pH of the pulp was maintained at the desired level by adding sulphuric acid.

Sl. No.	Particulars of addition	Condansate Water with Iron in it		Process water without iron in it	
		Brightness %	Yellow-ness,%	Brightness %	Yellow-ness,%
1.	Blank unbeaten pulp	89.3	4.5	86.6	5
2.	Beaten pulp	77.1	8.7	75.9	8 6
3.	P + R	80 3	5 7	76.5	7.9
4.	P + A	70.5	13.7	69.6	12.2
5.	P + R + A	72.1	12.6	70.1	12.3
6.	P + E	79.8	6 1	77.2	7.9
7.	P + R + A + F	72.6	12 2	76.3	10.0
8.	P + T + R + A + F				
	pH				
	7.5	82	2.8	84 3	Nil
	7.0	83.6	1.3	82.9	1.1
	6.5	81.2	3.0	82.9	Nil
	6.0	80 3	3.1	82.4	1.9
	5.5	77.7	6.2	77.3	5.8
	5.0	78.5	6.4	77.2	5.5
	4.5	80	3.5	77.2	6.5
	4.0	80	5.9	76.2	6.0

TABLE 1-A

THE EFFECT OF PROCESS WATER ON DULLING THE SHADE OF PULP

Sl.	Particulars	Imported Pulp				Bleached Bamboo Pulp			
		Condensate **		Process Water*		Condensate **		Process Water*	
		B	Y	B	Y	B	Y	B	Y
1.	Pulp before beating	85 6	3 0	81.5	7.6	65.0	16.8	65.1	24.5
2.	Pulp after beating	81.4	3.6	74.3	10.2	58.4	15 3	62.2	20.7
3.	P + R	83.2	2.5	73.3	10.1	63.3	17.5	66.7	20.3
4.	P + A	75.4	8.1	79.1	14.1	54.2	26.8	58.1	25.7
5.	P + T	86.2	7.9	76.2	8.4	64.1	20.5	65.7	16.3
6.	P + R + A	74.3	9.6	69.2	12.9	56.7	19.1	61.2	21.2
7.	P + T + R + A	75.2	6.6	72.2	7.4	59.8	12.3	60.0	23.3

Legend : B—Brightness percent, Y—Yellowness percent,
P—Pulp, A–Alum, T—Tinopal, R—Rosin.
*The process water contaminated.
**Condensate had traces of iron.

In the experiment studied, the extent to which the pulp loses its brightness is made clear by using distilled water and process water. In these two series, the proportion of each sizing chemical was in the normal dosage used in the stock preparation.

3.0 The brightness and yellowness of pulp:

The brightness as well as yellowness of pulp do contribute to the shade variation as well. There is considerable variation in the yellowness of bleached pulp at the same level of brightness. This would also make the pulp shade dull and the addition of brightening agent or dye can improve marginally the shade.

3.1 Measurement of yellowness of pulp :—

Measurement of pulp brightness is normally carried out on conventional double beam spectro photometer or ELREPHO BRIGHTNESS METERS by using reference values at the blue filter (R-457) with a mono-chromatic value of 457 nm using trichromatic colour measurement systems ([2]), ([3]), the measurement of brightness and colour of a smooth surface is done using three primary filters at Red, Green and blue with values 595 nm, 557 nm and 457 nm repectively.

Reflectance values obtained through these filters are termed as Tristimulas values (ELREPHO Filters 9, 10 & 11 are called Tristimulas filters).

From these reflectance values, it is possible to estimate the whiteness and yellowness of any bleached pulp by using the equation ;

$$\text{Yellowness Index} : \frac{R-B}{G} \times 100$$

$$\text{Whiteness Index (W)} : 4\,B - 3\,G$$

The Yellowness in bleached pulp was measured for a weak at the final hypo washer and recorded as in Table-II.

TABLE 2

BRIGHTNESS AND YELLOWNESS IN BLEACHED PULP

Sl. No.	Brightness %		Yellowness %				
1,	64	Time	6.30 pm	10.30 am			
		Yellowness	14.1	23.8			
2.	67	Time	4.30 pm	4.30 am			
		Yellowness	20.8	21,4			
3.	68	Time	8.30 am	4.30 am			
		Yellowness	19.4	21 4			
4.	69	Time	8.30 am	4.30 pm	10.30 pm		
		Yellowness	19.4	18.2	17.4		
5.	70	Time	8.30 pm	8,30 pm	6.40 am		
		Yellowness	18.1	19.6	17.0		
6.	71	Time	8.30 pm	8.30 pm	12.30 pm	10.30 pm	
		Yellowness	18.1	19.6	15.9	16.7	
7.	72	Time	6,30 am	12 30 am	12,30 am		
		Yellowness	16.0	15.3	16.7		
8.	73	Time	6.30 am	10 30 am	2 30 pm	2.30 am	10.30 am
		Yellowness	16.0	15.1	17,9	11.8	16.0
9.	74	Time	2 30 am	2.30 pm	6 30 pm	8 30 pm	4.30 am
		Yellowness	14.4	16.2	18.3	15.6	13.4
10.	75	Time	10.30 am	10.30 am	12.30 pm	6 30 pm	8 30 pm
		Yellowness	13.7	14,5	15 1	10.7	11.6
11.	76	Time	12 30 am	2 30 am	6 30 pm	8 30 pm	
		Yellowuess	13.7	12.3	10 7	11.6	
12.	77	Time	6.30 pm	2.30 am	2.30 pm	6 30 pm	8.30 am
		Yellowness	13 5	12.3	11.9	6.6	10.6
13.	78	Time	8.30 am	2.30 pm	4.30 pm	2.30 am	10.30 pm
		Yellowness	12.9	10.4	8 9	11.2	13 2
14.	79	Time	2.30 pm	4.30 pm	8.30 pm	4.30 am	10.30 pm
		Yellowness	15 6	16.0	17.6	13 9	13.2
		Time	2.30 pm				
		Yellowness	10.2				

The reversion of colour or brightness instability of bleached pulp was also computed by an accelerated ageing test and using the formula :—

$$\text{P.C. No.} : \frac{(1 - R_b)^2 - (1 - R_a)^2 \times 100}{2 R_a - R_b}$$

Where Ra : Reflectance ($R\alpha$) before ageing at 105°C for 4 hrs.

Rb : Reflectance ($R\alpha$) after ageing at 105°C for 4 hrs.

Graphical relationship between yellowness index and Post colour No. for the observed brightness of pulps, is given in Fig. 6.

4.0 Process Water :

The process water pH, Hardness as well as contamination with organic & metallic salts has a cumulative effect in lowering the pulp brightness of pulp when processed with distilled water and process water. In addition to this, the high hardness and organic contaminants in water will increase the demand of sizing chemicals. The high dose of alum only makes the pulp dull again.

5.0 Variable Stock Dyeing

The dyes are extremely sensitive compounds. The final shade of pulp depends primarily upon all the sizing chemicals, filler and dyes added to the stock for achieving the desired shade as well as their sequence of addition during the pulp refining stages. Other major factors that contribute to the better colouring of paper are the pH, acidity in back water, temperature of dye dissolution and addition, pulp freeness, fillers in respect of their brightness level and the time and intensity of stock agitation in the mixing chest.

6.0 Technology of colouring fibre :

The basic dyes have no affinity to bleached fibres, which also contain electro-negative groups on the macromolecular chains. To create an atmosphere essential for fixing the dye on to the bleached fibre, it is required to have mordants like Tamol NOP. Alum also satisfies the purpose of fixing the dye to the fibre through "Lake Formation" [4], the mechanism being, breaking up of a barrier of electro negativity on pulp surface, enabling the concentrated layer of the dye to permeate into the fine layers of the beaten stock to impart a bright colour to the pulp.

It is also important to maintain the same order of addition of the dyes and chemicals for each batch of beaten stock in the mixing chest. In many cases for the same reason the dyestuff should be added before rosin and alum, except when it is desirable to retard the absorption of dye by the fibre, in which case it is sometimes advisable to add the dye-stuff after rosin. It is essential to give enough time for mixing the chemicals effectively with the stock to improve upon achieving the desired shade.

7.0 Effect of filler on stock dyeing :

Many common fillers have pronounced affinity for dye-stuffs. They absorb the same quantity of dye as the paper fibre and some have even greater adsorption limit Because the fillers tend to take up the dye as above, the colour of filled paper is generally weaker than it would be if no fillers were present. Thus it is essential to use filler with minimum absorptive power and it is necessary to follow an order of addition which reduces this effect to minimum. One way to do this is to add filler at the end as close to the sheet formation as possible. Talc and Titanium dioxide absorb maximum; with china clay and Kaolin the effect is moderate. However, the characteristics of absorption depend on the basic chemical structure of the dye used.

8.0 Dyeing Scheme followed here :

The sequence followed at our stock preparation unit in the dyeing of bleached pulp is as under :

Whitening agent and rosin are added to the raw bleached pulp as received in the receiving chest. The virgin pulp is refined with whitening agent and rosin and received in the mixing chest. Here, the desired dye in suitable concentration is added to the pulp and it is followed by the filler and finally the desired quantity of Alum. Even while the alum addition continues, the broke and back water are added to the chest to the desired level and the stock is kept agitated ready for being discharged for further processing. It is desirable that the pulp is kept well agitated in the chest and sufficient dwell time is given to the stock for fixing the dye. It is in the order of 30-45 minutes.

9.0 Modifications in thn sequence of Dyeing Stock :

From what has been discussed earlier about the technology and mechanism of dyeing stock, it is evident that in such a scheme as above there are chances for the uneven distribution of the dye on the fibre, resulting in mottling and absorption by the filler resulting in a dull shade and often a non-uniformity in the shade of stock between different chests cleared during the day. This could have been one of the many reasons for the shade variation in paper. To minimise the shade variation at this level, it was felt apt to change the sequence of the dye and chemical addition to the bleached pulp.

Accordingly, the following modes of chemical additions were tried on an experimental basis in the laboratory with Victoria blue and Paper blue. The dyestufl was added immediately following whitening agent, rosin and alum addition to the pulp and allowed to mix thoroughly. After a minute or so the filler was added and the sheets were formed. The tendency of the filler absorbing the dye was minimised as also there was no molting effect experienced in this addition.

The effective shade of the paper made by this mode of dye addition was deep in colour and the tables 3 & 4 campare the Tristimulus values and the chromaticity co-ordinates for each mode of addition followed in the experiments. Sequence of additiou of whitening agent to the pulp is immaterial as a consequence of the above experiments. The addition of alum immediately following rosin improves the dye fixing on to the fibre in comparison with the sequence in which alum is added at the end as shown in the enclosed figures 1-4. The shades were quite uniform and brilliant.

Another set of a two dyes, namely Victoria Blue and Rhodamine were tried in combinations used for Maplitho shades in the paper machine.

A typical combination of the dyes and chemicals used in the plant during the period of study is given hereunder :

Basis 100 parts of pulp.	
Victoria Blue	0.05%
Rhodamine	0.02%
Ultra phore	0.15%
Rosin	1%
Alum	5%
Filler	8-10%

The pulp brightness was 81%.

The directional reflectance of each pulp after the addition of the chemicals, and dyes were cerefully measured in an ELREPHO reflectance photometer. The tristimulus values and Trichromatic co-ordinates which define the colour of the paper made are recorded in Table 5. There is a marked change in the colour of the paper made and the directional reflectance curves for all these shades are recorded in Figures 5.

The sequence of adding whitening agent, rosin and alum followed by dye and filler is deep in colour compared to the addition in which alum is added at the end or in which dye and filler are mixed and then added to the stock.

After considerable experimental work, this sequence was tried in the stock preparation on the M.F. machine over a period of nearly three weeks. No marked deterioration in the quality of shade was observed during this period.

Table—3

DIFFERENT MODES OF CHEMICAL ADDITION TO REFINED STOCK LEGEND OF CHEMICALS AND DYES

1.

A	Alum
B	Rosin
WA	Whitening Agent
F	Filler
D	Dye.

2. **Concentrations :**

Basis : 100 parts of pulp

Paper blue/Victoria blue	0.024%
Ultraphore/Tinopal	0 72 %
Rosin	1 %
Alum	4 %
Filler	8 %

3. **Sequence of addition :**

A	B	C	D	E	F
R	R	R	R	R	R
A	D	WA	A	A	
D	WA	VB	WA	WA	D&F
WA	F	F	D	D&F	WA
F	A	A	F		A

4. **Subscript Notations :**

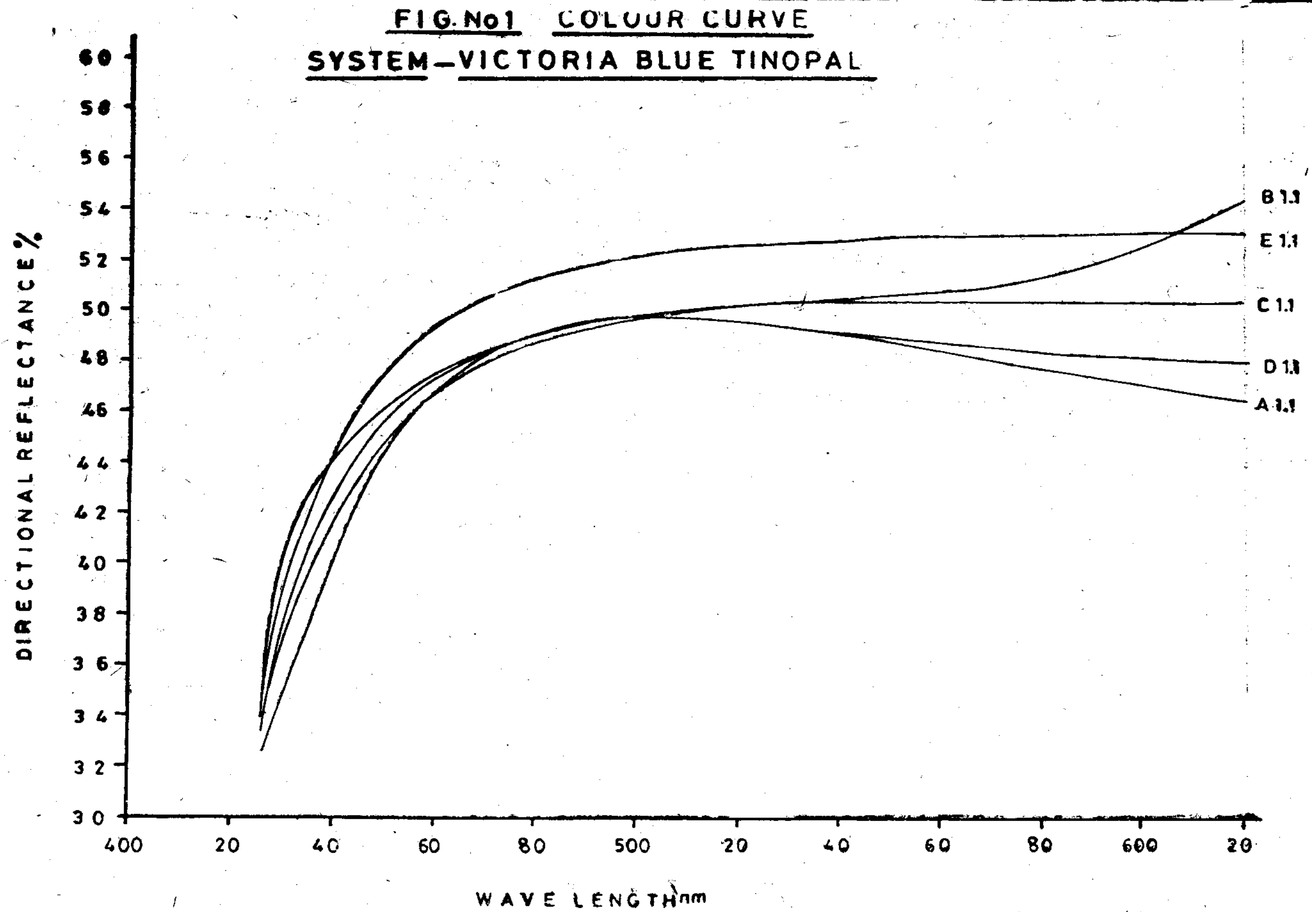
1.1. Victoria blue and Tinopal
1.2. Victoria blue and Ultraphore
2.1. Paper blue and Ultraphore
2.2. Paper blue and Tinopal.

Table—4

TRISTIMULUS VALUES AND CHROMETICITY CO-ORDINATES FOR DIFFERENT MODES OF ADDITION OF DYES, CHEMICALS AND WHITENING AGENTS

Sl. No.	Sequence	Tristimulus Values			Chromaticity Co-ordinates	
		X	Y	Z	X	Y
1.	A1.1	47 15	48.5	54.6	0.314	0.323
2.	B1 1	49 1	50.9	54.4	0.318	0 330
3.	C1.1	48.75	50 7	55.9	0.320	0 326
4.	D1.1	47	48.9	54	0.313	0.326
5.	E1.1	51 2	53 1	58	0 316	0 327
6.	F1 1	47.3	49	53 5	0.316	0.327
7.	A1.2	48 45	50.7	56 2	0.312	0 326
8.	B1.2	47.1	49.2	55.5	0.310	0 327
9.	C1.2	49 6	51.3	60	0.308	0.319
10.	D1.2	47.7	49.2	55	0.314	9.319
11.	E1.2	49 2	51.4	58	0.310	0.324
12	F1.2	52.15	53.9	60	0 314	0.325
13.	A2.1	54.6	56 5	61	0.317	0.328
14.	B2 1	54 95	56 3	63 2	0.315	0 323
15.	C2 1	51.15	53.9	56 5	0.321	0.322
16.	D2 1	54.35	56.1	62	0.315	0 325
17.	E2.1	52.15	53.7	48.8	0.317	0 326
18.	F2 1	54.72	56.1	49.1	0.322	0.330
19.	A2 2	50 64	51.7	55.2	0.322	0.328
20.	B2.2	47.76	48.7	52.2	0.321	0.327
21.	C2 2	48.51	49.1	53.2	0.322	0 326
22.	D2.2	50.65	52 1	61.2	0.309	0.318
23.	E2.2	50.65	51.6	57.8	0.316	0.322
24.	F2 2	49.65	50 7	54.5	0.301	0.327

FIG.No1 COLOUR CURVE
SYSTEM—VICTORIA BLUE TINOPAL



TABLE—5

COMPARISON OF TRISTIMULUS VALUES AND CHROMATICITY CO-ORDINATES FOR DIFFERENT MODES OF ADDING DYES

System: Victoria Blue-Rhodamine And Ultraphore

Legend: VB—Victoria blue, RH—Rhodamine, UP—Ultraphore, T—Talc, A—Alum, R—Rosin.

1. **Sequence:**

A	B	C	D	E	F	G	H	I
R A VB RH	R A UP	UP R A	UP R VB RH	R UP VB RH	R A UP	R UP VB&F mixed RH	UP R VB&F mixed RH	UP R A
UP	VB RH	VB RH	F	F	VB&F mixed RH	A	A	VB&F mxd RH
F	F	F	A	A				

2. **Tristimulus Values and Chromaticity Co-ordinates:**

Sample	Tristimulus values			Chromaticity Co-ordinates	
	X	Y	Z	X	Y
A	53.72	54.8	54.11	0.3305	0.337
B	52.21	52 9	51.62	0.3323	0 3376
C	53.25	54.1	53.15	0 3318	0 3371
D	55 16	55 7	55.27	0.3321	0 3354
E	55.24	56 0	55.4	0.3325	0 3361
F	54.23	:4 8	54.34	0.3328	0 3353
G	55 16	55.9	55.29	0.3325	0.3359
H	55.2	55.9	55.51	0.3313	0 3355
I	54.48	55.4	53 98	0.3324	0 3380

FIG. No 2 COLOUR CURVE

SYSTEM— VICTORIA BLUE ULTRAPHORE

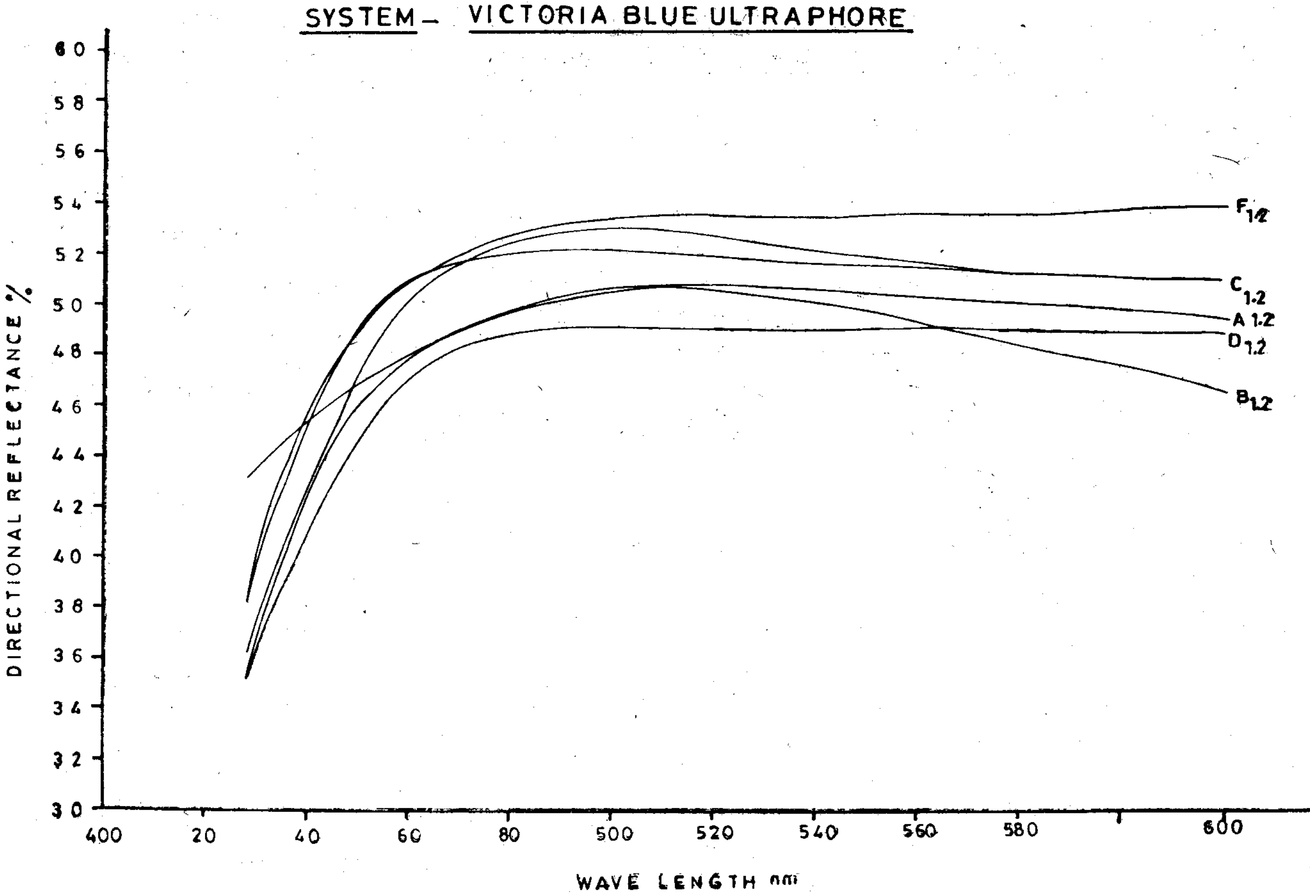


FIG No 3 COLOUR CURVE

SYSTEM PAPER BLUE ULTRAPHORE

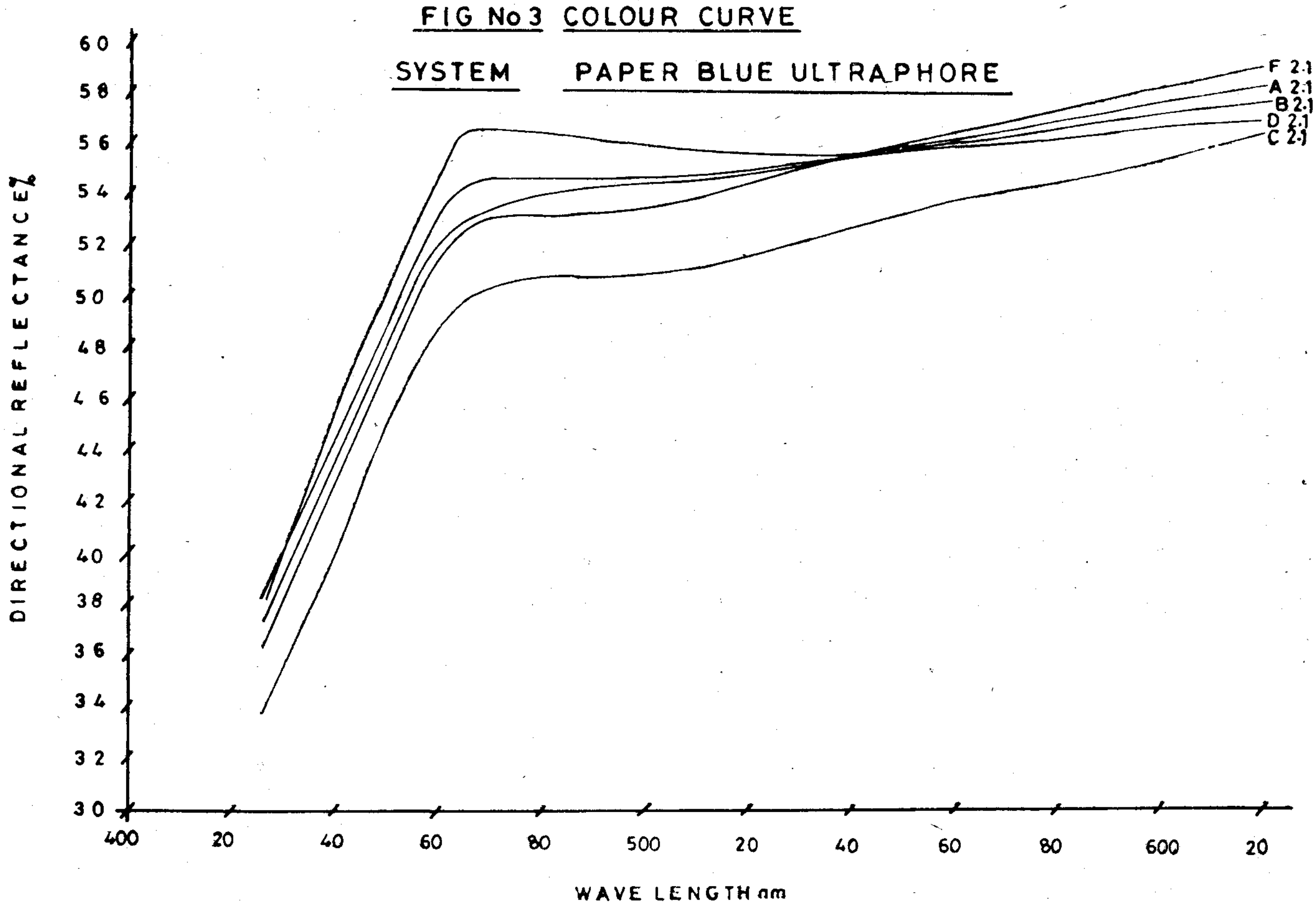
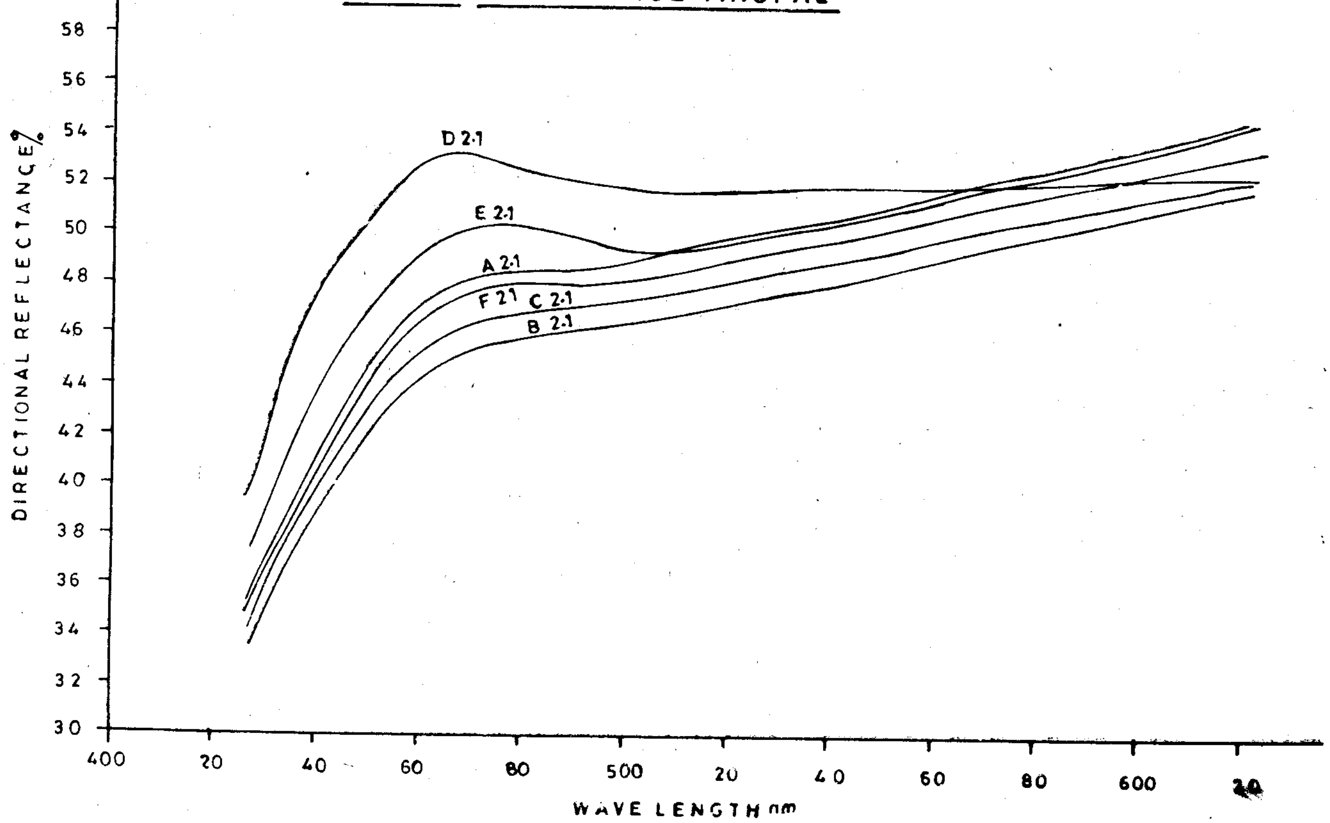
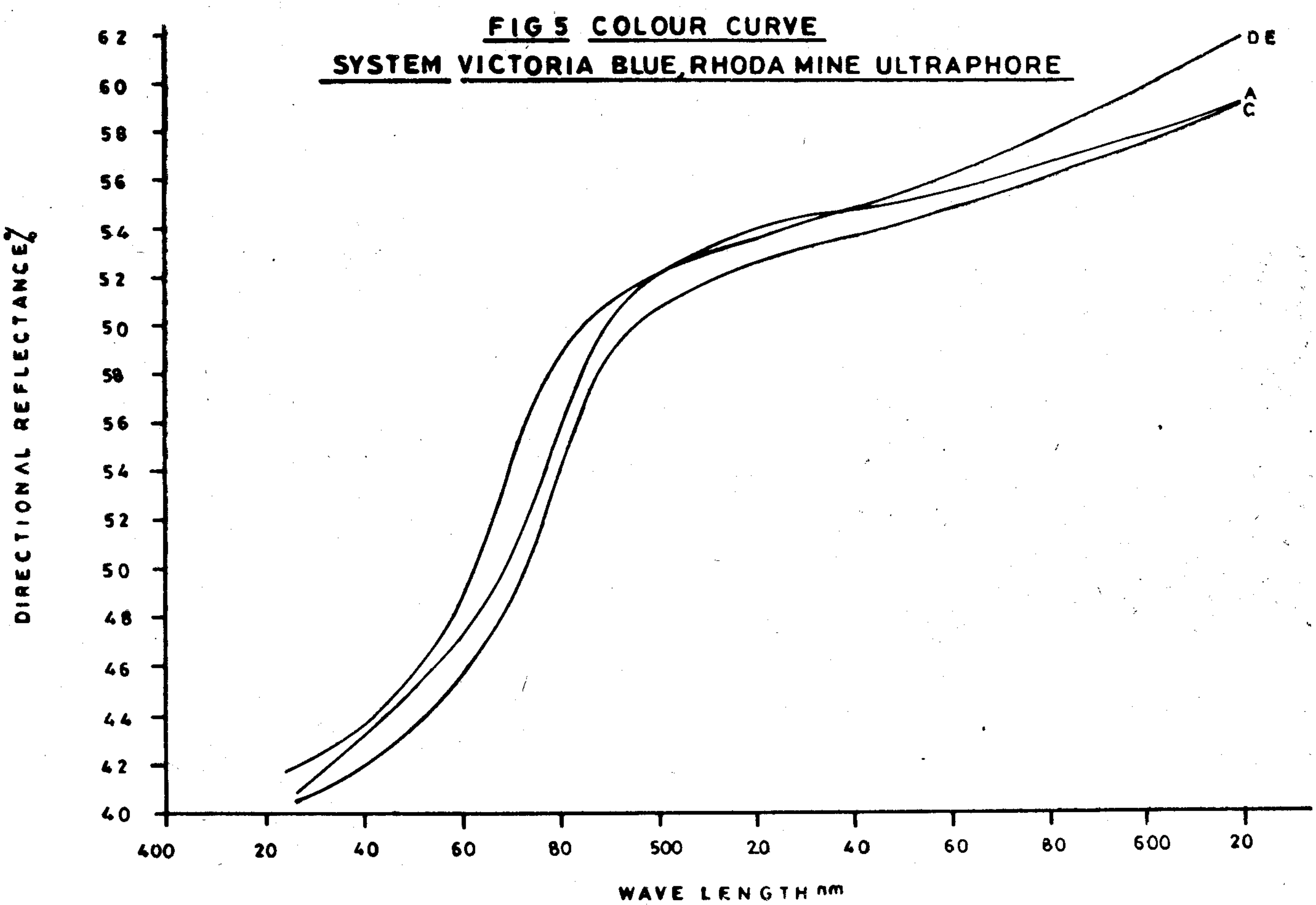


FIG. 4 COLOUR CURVE

SYSTEM_PAPER BLUE TINOPAL





10.0 Advantges of the new mode of addition :

i) The colour intensity of pulp is high for the same quantity of dye added, and hence saving in cost.

ii) No mottling effect in the coloured pulp.

iii) The addition of filler can be ,increased at ease without fear that it may affect the shade of paper which is dyed already.

iv) Minimum twosidedness in the heavily dyed papers.

v) Probably minimum shade variation in the paper.

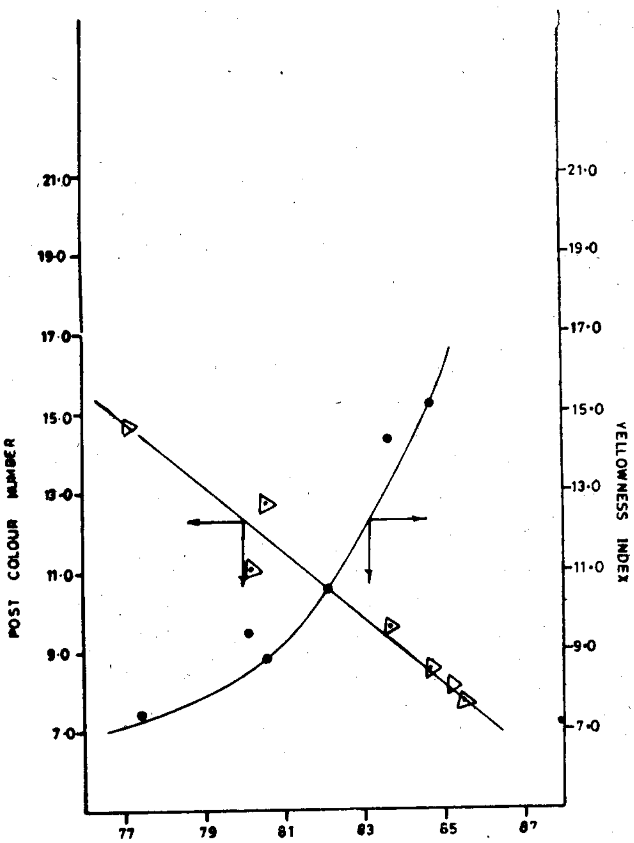
vi) Fastness of the dye to heat on the dryers as the dye is better fixed to the pulp.

11.0 Colour maching :

The variation in shade can be minimised when this method of addition is followed by matching the colour reflectance spectrum for eaeh dye or dye combinations used. We can match and define the colour combinations by computing the tristimulus values, chromaticity co-ordinates dominant wave length and the excitation purity of the dye by comparing with the standard shade we want to derive from the dye used([5],[6]). The interpretation of the detailed method of comparison of dye shades are in the final stage and will be included in our continuing report on shade variation.

The tristimulus values can be now measured directly through either technibrite or data colour spectrophotometers. By using these instruments the colour /shade matching can be done instantly and accurately.

FIG.6 RELATION BETWEEN YELLOWNESS INDEX AND POSTCOLOUR NUMBER



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