Troubleshooting

Presented by:
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"Recent Developments in Dye Process Monitoring and Control"
Raleigh, North Carolina

Title: <u>Trouble shooting</u>

Abstract: In this project we have developed data acquisition systems, dyeing models, etc. which can be used for several purposes, notably research, control, and diagnostic evaluation of dye recipes, raw materials and processes. This talk presents practical uses of these developments, such as why fiber reactive dyeings sometimes fail to repeat, and how to set up recipes that avoid lot-to-lot shade variations.

By: Brent Smith

Our data acquisition system can provide a method for real-time process analysis, and therefore it can often pinpoint the exact causes of poor shade repeats or other defects.

Some relevant publications showing the potential for this are attached. This talk will include examples from those publications and other experiences over the last few years in this project.

Batch Dye Process Control Starts with Process Design and Dye / Chemical Selection

Process Design Considerations ...

Timing of events

Temperature profile

Dyeing temperature

pH

Salt

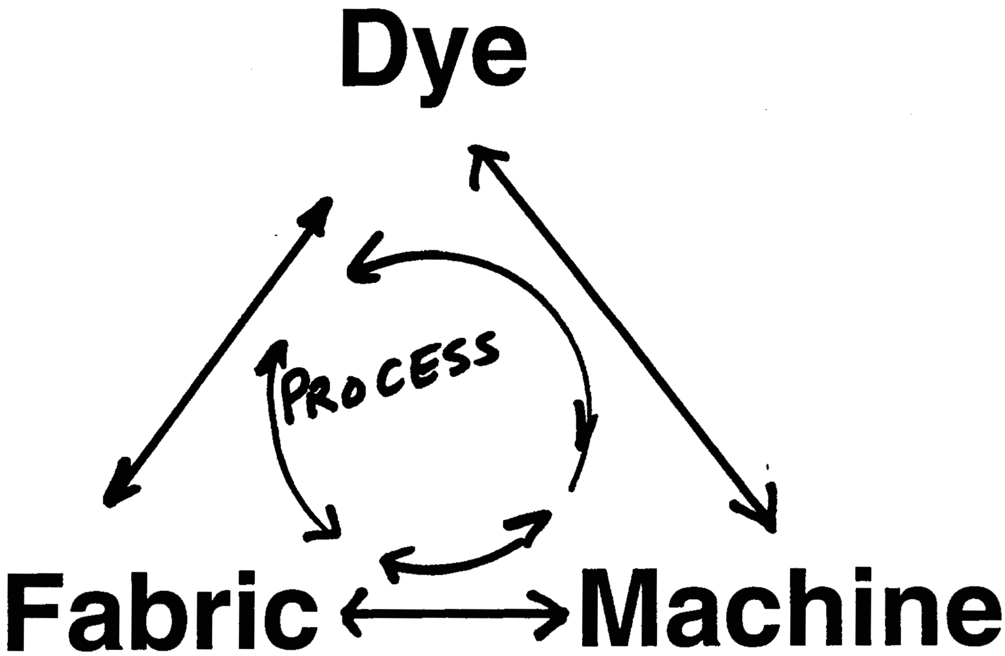
Bath ratio

Stirring/Contact

... (machine dependent)

Consider as an example ...

DIRECT DYES on COTTON


Dye
PROCESS
Fabric
Machine

Applications Considerations for Direct Dyes

<u>Quantifiable with DARG system</u>

Affinity

Controllability
- Salt
- Temperature
- pH

Rate of Exhaustion

- Diffusion Coefficient
- Time of half dyeing

Stability to Reduction

Aggregation and Dye/Dye Interaction

<u>Other</u>

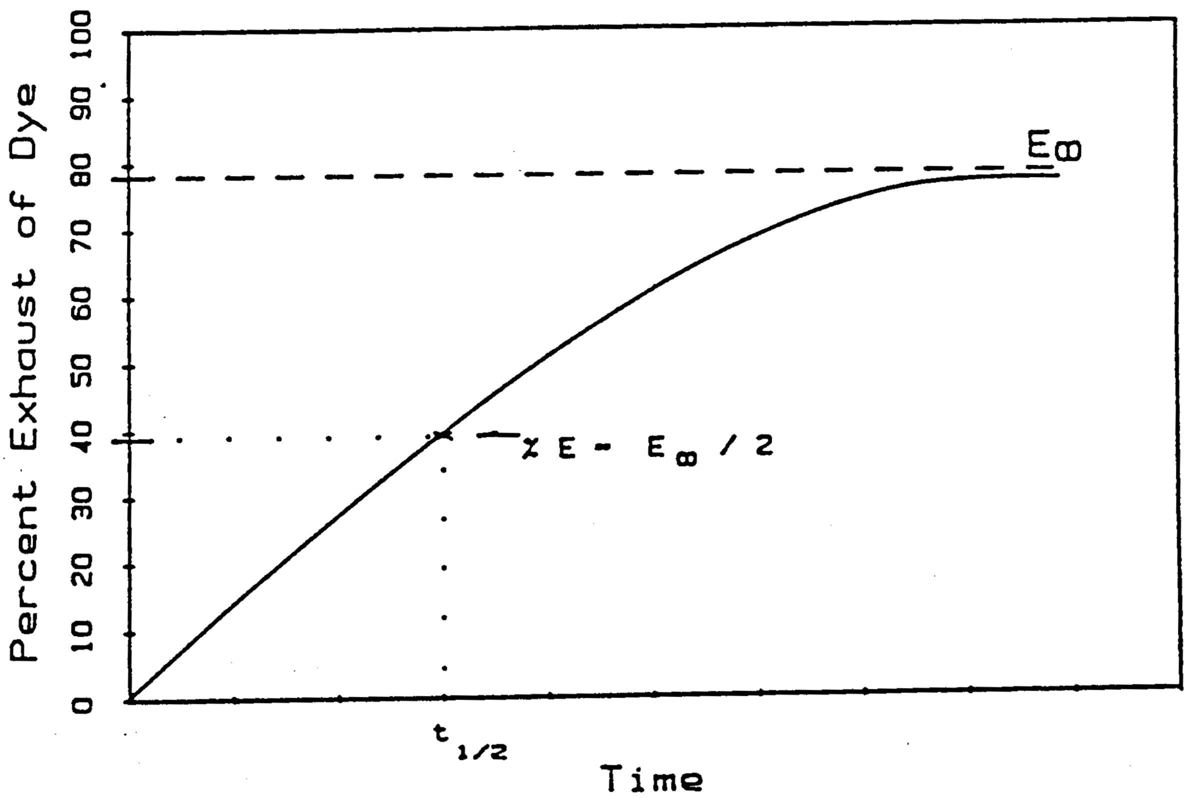
Cost
Fixation method
Cross staining
Fastness, ...

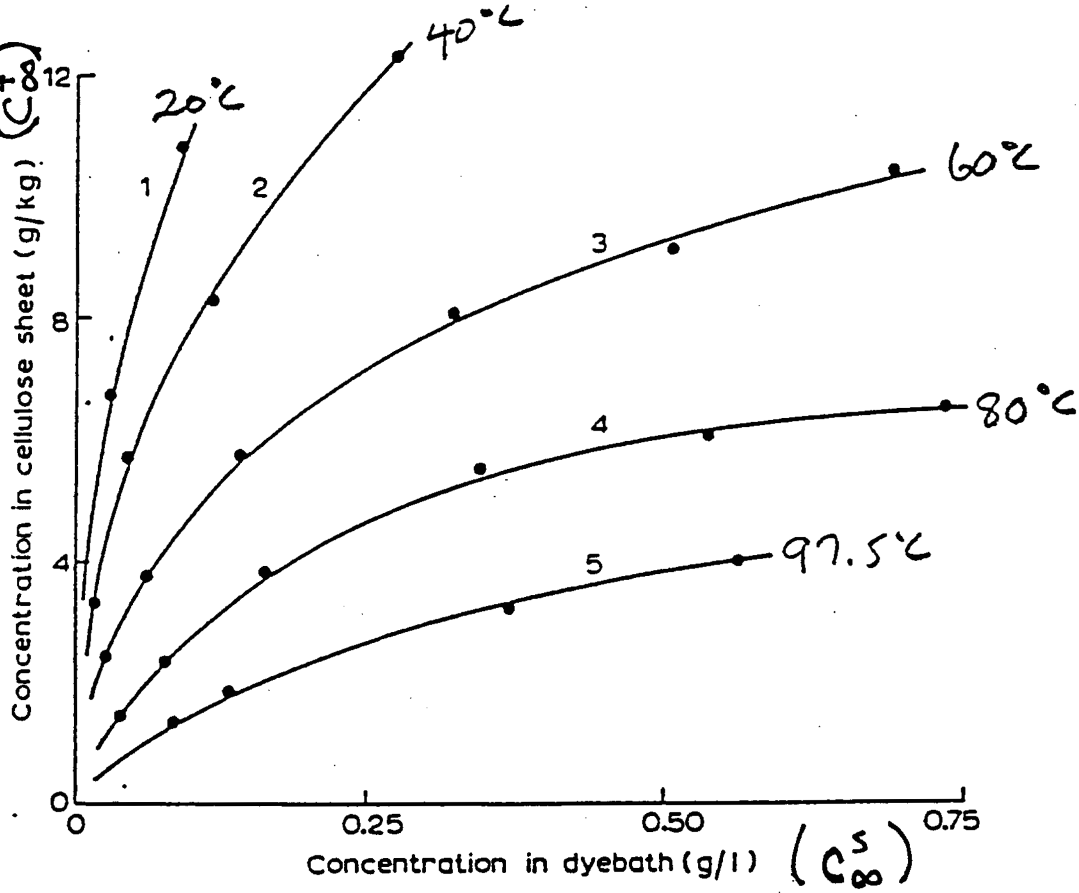
Specific Characteristics of Dyes Which Dictate Process Design

Dye Characteristic	Process Design Factor
Temp Sensitivity	Temp setpoints Rate of heat/cool Time/temp profile
Salt Sensitivity	Salt amounts Dosing rates Salt addition procedure
Dyeing Rate	Time/temp profile Contact/stirring Machine speed Rate of heat/cool Compatible combinations
Affinity	Dye selection Compatible combinations Washing/fixation methods
Behavior of Mixtures	Dye selection

Dyeing Exhaust Curve

Based on Amount of Dye in the Fiber





Effect of temperature on adsorption of Chrysophenine G on cellulose sheet in the presence of 1 g/l sodium chloride 1, 20° C; 2, 40° C; 3, 60° C; 4, 80° C; 5, 97.5° C.

CI DIRECT YELLOW 12

Temperature Sensitivity of Dyes

Process Considerations:

Temperature setpoints
Rate of heat/cool
Time/temperature profile
Compatible combinations

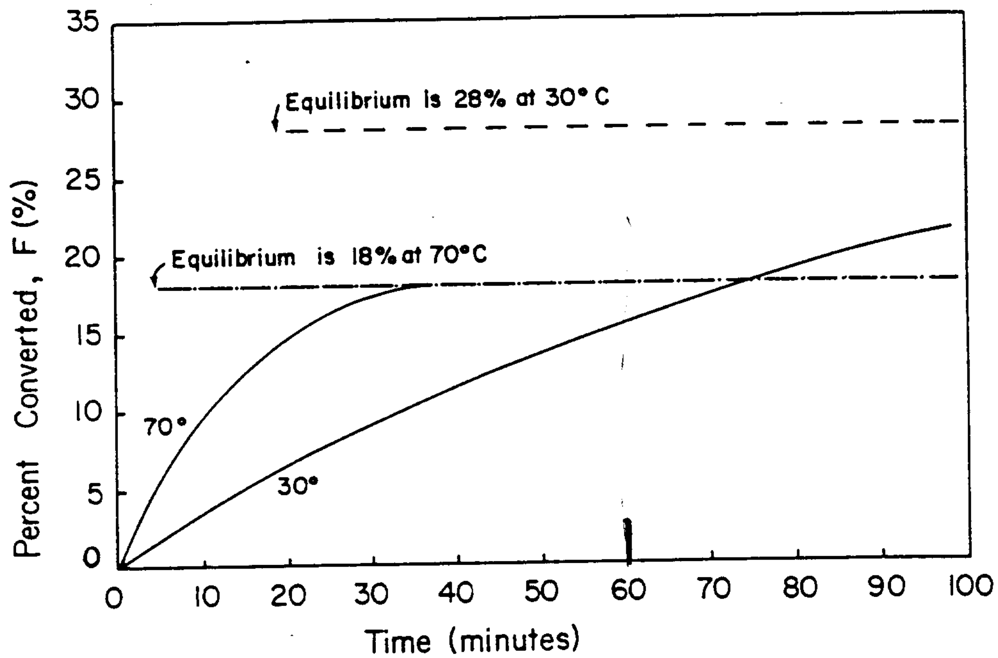
Effects: As temperature increases ...

Dyeing occurs more rapidly
Diffusion rate increases
Possible reduction of dye increases
Penetration of fabric structure increases
Better leveling
Faster "strike"
Equilibrium exhaust decreases

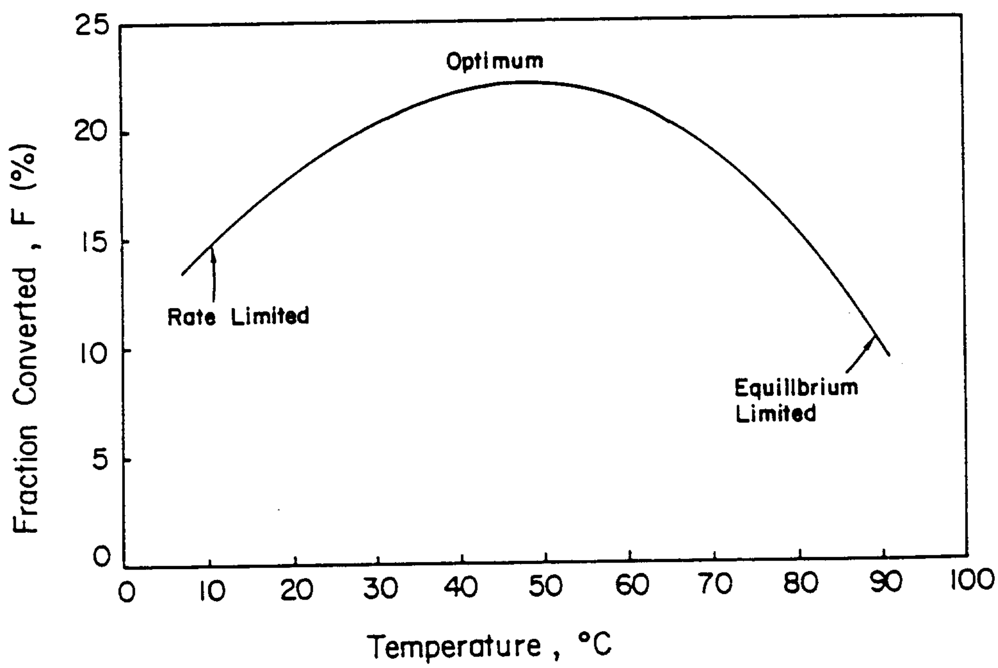
$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^\circ}{R} \approx \text{a constant} > 0$$

If $\Delta H^\circ < 0$, then K decreases with increasing T (as in this case)

These effects have been widely modelled and studied in the past.



Conversion as a function of time at 30 and 70 °C.



Fraction conversion in 1 h vs. temperature of reaction.

(of dye in [illegible]

Dye Name		Chemical Type	M.W.	temp °C max affinity
Yellow 4	√	1,5	624	—
Yellow 6	√	5	470	—
Yellow 7		4	591	—
Yellow 8	√	1,4	530	—
Yellow 11	√	5	474	70
Yellow 12	√	1,5	680	40
Yellow 19		1,5	680	—
Yellow 20		1	554	—
Yellow 26		1	584	50
Yellow 27	√	1,4	662	35
Yellow 28	√	1,4	680	80
Yellow 29	√	1,4	946	100
Yellow 44	√	1	634	50
Yellow 50	√	1	1004	60
Yellow 106	√	5	—	95
Orange 1		1	642	50
Orange 8	√	1	635	70
Orange 15	√		416	80
Orange 26	√	1	804	80
Orange 29	√	1	870	80
Orange 34	√	1,5	753	80
Orange 37	√	1,5	783	100
Orange 39	√	1,5	739	80
Orange 102	√	1	870	—
Red 1	√	1	651	90
Red 2	√	1	772	80
Red 7		1	804	80
Red 10		1	745	80
Red 16	√	1	685	60
Red 17		1	745	50
Red 20		1,4	657	60
Red 23	√	1	861	90
Red 24	√	1	950	100
Red 26	√	1	1010	100
Red 28	√	1	744	80
Red 31	√	1	761	50
Red [illegible]		1	—	—
Re[illegible]	√	1	700	80
Red 29	√	1	728	80

Dye Name		Chemical Type	M.W.	Metal	temp °C max affinity
Red 72	√	1	1009	Ø	100
Red 75	√	1	1038	Ø	80
Red 76	√	1,5	813	Ø	100
Red 79	√	1	1096	Ø	90
Red 80	√	1	1420	Ø	100
Red 81	√	1	699	Ø	60
Red 83	√	1	1068	Ø	100
Red 153	√	1	714	Ø	60
Violet 1	√	1	776	Ø	100
Violet 9	√	1	715	Ø	40
Violet 22		1	848	Ø	—
Violet 47	√	1	1048	Ø	90
Violet 48	√	1	979	Ø	100
Violet 51	√	1	743	Ø	40
Violet 66	√	1	951	Ø	—
Blue 1	√	1	1040	Ø	70
Blue 6	√	1	980	Ø	60
Blue 8		1	806	Ø	90
Blue 14	√	1	1008	Ø	70
Blue 21		1	891	Ø	90
Blue 25	√	1	1010	Ø	70
Blue 26		1	1102	Ø	100
Blue 27		1	876	Ø	—
Blue 55		1	921	Ø	80
Blue 67	√	1	907	Ø	80
Blue 71	√	1	1125	Ø	90
Blue 75	√	1	1127	Ø	100
Blue 76	√	1	1040	Ø	70
Blue 78	√	1	1127	Ø	95
Blue 80	√	1	—	—	100
Blue 86	√	2	779.5	1	—
Blue 98	√	1	971	Ø	100
Blue 106	√	3	741	Ø	—
Blue 108	√	3	898	Ø	—
Blue 120.1	√	1	949	Ø	—
Blue 218	√	1	1040	Ø	95

Dye Name		Chemical Type	M.W.	temp ° max affi
Green 1	√	1	791	80
Green 6	√	1	836	80
Green 8		1	902	80
Green 11		1	788	60
Green 26	√	1	1344	100
Green 28	√	1,6	992	80
Brown 1	√	1	680	100
Brown 2	√	1	651	70
Brown 6		1	682	100
Brown 25		1	991	90
Brown 29		1,5	946	—
Brown 31	√	1	1165	100
Brown 58		1	679	80
Brown 74		1	1886	—
Brown 95	√	1	698	100
Black 3		1	567	100
Black 4	√	1	819	90
Black 9	√	1	816	100
Black 22	√	1	1131	100
Black 38		1	805	—
Black 51	√	1	665	40
Black 56		1	947	80
Black 74		1	1227	100
Black 80	√	1	978	90
Black 91	√	1	926	—
Black 166	√	1	—	—

1 = azo
2 = phthalocyanine
3 = dioxazine
4 = thiazole
5 = stilbene
6 = anthraquinone

Temperature of Maximum Affinity for Several Direct Dyes

40 C	Y12, Y27 (35C), V9, V51, Blk51
50 C	Y26, Y44, O1, R17, R31
60 C	Y50, R16, R20, R81, R153, Blu6, G11
70 C	Y11, O8, Blu1, Blu14, Blu25, Blu76, Brn2
80 C	Y28, O15, O26, O29, O34, O39, R2, R7, R10, R28, R37, R39, Blu55, Blu67, G1, G6, G8, G28, Brn58, Blk56
90 C	R1, R23, R79, V47, Blu8, Blu21, Blu71, Brn25, Blk4, Blk80
100 C	Y29, Y106 (95C), O37, R24, R26, R72, R75, R76, R80, R83, V1, V48, Blu26, Blu75, Blu78 (95C), Blu80, Blu98, Blu218 (95C), G26, Brn1, Brn6, Brn31, Brn95, Blk3, Blk9, Blk22, Blk74

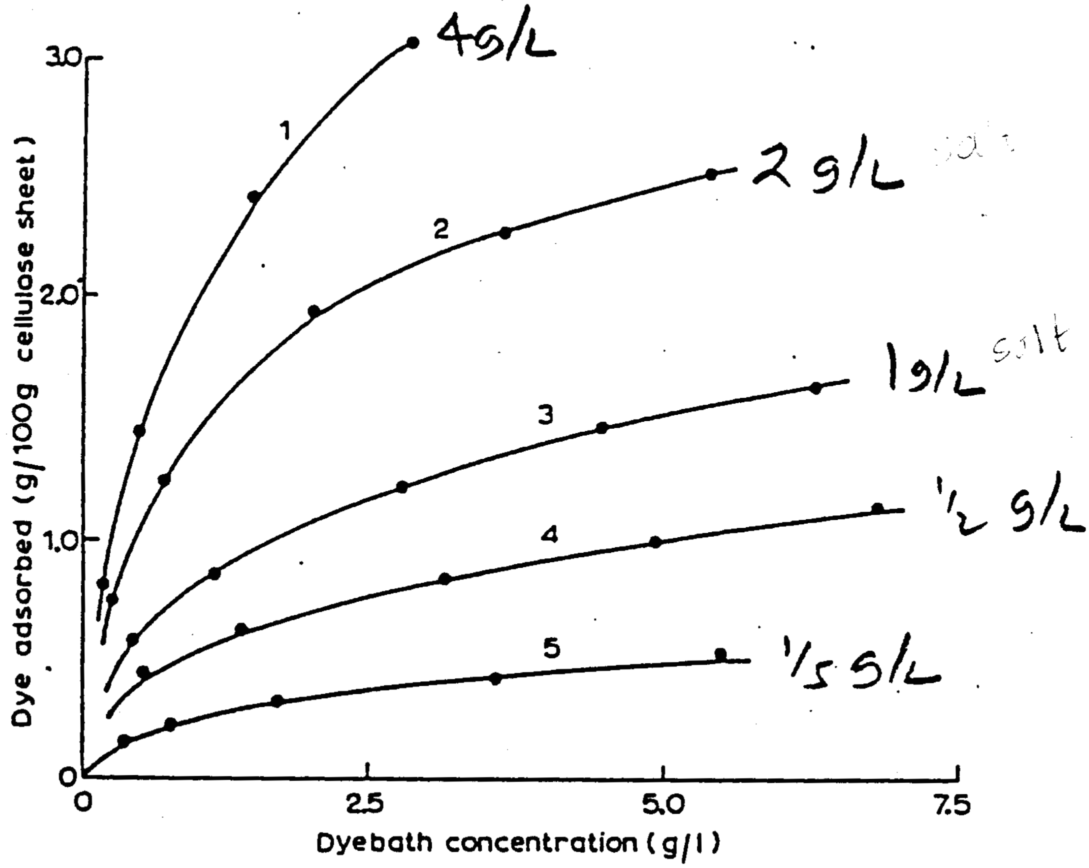
Salt Sensitivity of Dyes

<u>Process Considerations:</u>

Salt amounts
Dosing rates
Salt addition procedure
Appropriate combination

<u>Effects:</u> The role of salt in direct dyeing ...

Increases solution ionic strength
Increases dye affinity for substrate
Changes (+/-) dye diffusion coefficient
Disrupts water structure near ionic dyes
Breaks "icebergs"
Decreases hydration of dye
Increases potential for dye aggregation
Na^+ can partition for electrical neutrality
Offsets negative zeta potential of fiber
Salts out dye (common ion effect)
Increases dye chemical potential/activity



Adsorption isotherms of Chrysophenine G on cellulose sheet at 40°C and varying salt concentrations [9]. 1, 4.0 g/l NaCl, 2, 2.0 g/l NaCl; 3, 1.0 g/l NaCl; 4, 0.5 g/l NaCl; 5, 0.2 g/l NaCl. YELLOW 12

SALT

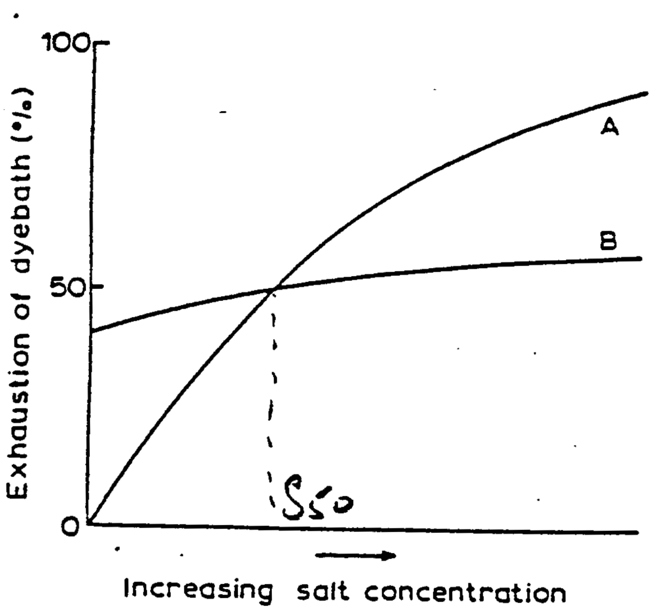
Amount of Salt Generally Used With Direct and Reactive Dyes

Depth of Shade	Direct	Reactive
Pastel/Light up to 0.5% – 1.5%	2.5 – 7.5 g/l	30 – 60 g/l
Medium 1.0% – 2.5%	7.5 – 12.5 g/l	60 – 80 g/l
Dark above 2.5%	12.5 – 20 g/l	80 – 100 g/l

Salt required to produce 50% exhaustion of direct dyes [9]

Dye	Salt addition for 50% exhaustion (% on wt. of fibre)
Chlorazol Brown MS	0
Benzopurpurine 10B Red 7	0
Benzopurpurine 4B Red 2	0.2
Chlorazol Dark Green PLS GRN 1	0.4
Diazo Black OT	1.0
Melantherine BH	1.0
Chlorazol Green GS Green 8	1.2
Chlorazol Fast Yellow 5GKS	2.0
Oxyphenine GG	2.0
Primuline AS	2.0
Trisulphon Brown B - Brown 31	2.0
Chlorazol Fast Pink BKS	2.0
Diphenyl Brilliant Blue FF	2.0
Diazo Brilliant Orange GR	4.0
Durazol Red 2BS Red 81	5.0
Benzo Fast Helio 4BL	5.4
Chlorazol Fast Eosine B	7.0
Benzo Fast Yellow RL	8.5
Benzo Fast Yellow 4GL	8.5
Chrysophenine G Yell 12	13.0
Rosanthrene Pink	16.0
Rosanthrene Violet 5R	30.0

30:1 Liquor ratio



← 2 dyes with same amt of salt required to produce 50% exhaust ...

A is salt ~~50%~~ sensitive

B is not

also Vickerstaff

Boulton JSDC, 1934, p383

2g/L 6g/L

Sil liquor ratio

Effects of salt on time & E∞ @ Silk 90°C Vickerstaff

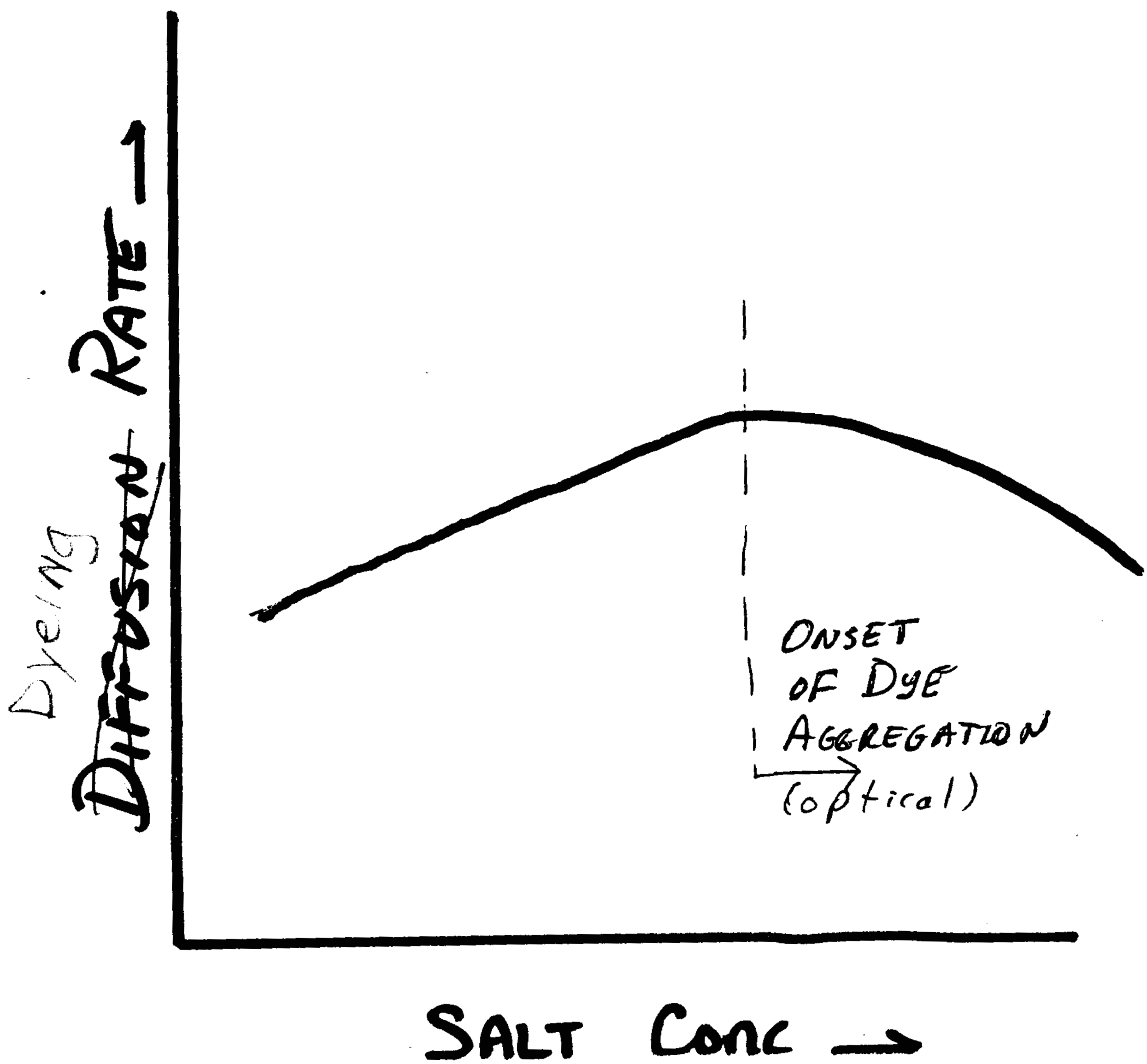
Dye	Depth of Shade (%)	Equilibrium Exhaustion (%)			$t_{\frac{1}{2}}$ (min.)		
		0% Na_2SO_4	1% Na_2SO_4	3% Na_2SO_4	0% Na_2SO_4	1% Na_2SO_4	3% Na_2SO_4
Durazol Fast Yellow GR 200	0·5	65·0	83·0	92·0	1·5	1·1	0·5
Durazol Fast Yellow G 400	0·5	87·0	96·5	99·0	0·4	0·2	0·1
Durazol Fast Yellow 6GS	1·5	78·0	82·1	85·1	0·3	0·2	0·1
Chlorazol Yellow 6GS ...	1·0	—	—	—	—	—	—
Chrysophenine G 200 ...	0·5	39·0	67·0	82·0	0·3	0·2	0·2
Durazol Fast Orange 2G 125	1·0	52·0	73·0	82·0	1·6	1·1	0·4
Chlorazol Fast Orange D 125	1·5	20·0	35·0	46·5	3·5	2·9	1·0
Durazol Fast Orange 4R 150	0·5	42·5	75·0	84·0	3·7	0·7	0·4
Chlorazol Fast Orange R 150	0·5	90·0	93·0	95·0	1·0	0·2	0·1
Chlorazol Orange PO 150 ...	0·5	80·0	92·0	95·0	1·0	0·5	0·1
Chlorazol Brown LF 150 ...	1·5	70·0	77·0	83·0	1·0	0·6	0·4
Chlorazol Brown M 150 ...	0·5	89·0	95·0	97·5	0·8	0·2	0·1
Chlorazol Catechine B 125...	1·5	26·5	30·5	40·0	1·5	1·2	1·0
Chlorazol Catechine GR 150	1·5	55·0	64·0	70·0	0·9	0·8	0·6
Chlorazol Drab RH 125 ...	1·0	77·0	84·0	91·0	1·0	0·6	0·4
Chlorazol Orange Brown X 150	1·0	88·5	92·5	95·0	1·7	1·3	0·8
Chlorazol Bordeaux BS ...	1·0	92·0	95·5	98·0	0·9	0·4	0·2
Chlorazol Bordeaux 6B 150	0·5	81·0	92·5	95·8	0·2	0·1	0·1
Chlorazol Fast Pink BK 200	0·5	32·0	59·0	82·5	6·5	0·9	0·6
Chlorazol Fast Red F 125...	1·0	74·0	89·5	95·0	1·0	0·6	0·2
Durazol Red 2B 150 ...	1·0	41·0	63·0	83·0	0·5	0·2	0·2
Chlorazol Fast Scarlet 4BAS	1·0	77·5	90·5	94·5	1·8	0·9	0·4
Chlorazol Fast Scarlet 4B 150	0·5	95·0	97·5	98·5	0·9	0·2	0·1
Chlorazol Fast Scarlet 8B 125	1·0	83·0	93·0	96·5	2·0	1·0	0·4
Chlorazol Fast Scarlet GS...	1·0	75·0	85·0	91·5	1·5	0·8	0·6
Durazol Fast Rubine B 150	1·0	44·0	75·0	87·0	4·0	2·0	0·8
Durazol Helio B 200 ...	0·5	65·25	86·0	91·5	0·7	0·3	0·2
Chlorazol Fast Helio 2RK 200	0·5	61·0	82·0	90·5	0·3	0·2	0·2
Chlorazol Violet N 125 ...	0·5	73·0	90·5	95·0	2·1	0·7	0·4
Durazol Fast Violet 2BS ...	1·0	10·5	27·5	53·5	2·1	1·0	0·7
Chlorazol Blue B 200 ...	1·0	66·0	81·0	90·0	0·9	0·4	0·3
Chlorazol Blue G 150 ...	1·0	36·0	51·0	71·0	0·6	0·3	0·3
Durazol Fast Blue 3R 200	1·0	41·5	73·0	91·5	1·2	1·5	0·5
Durazol Fast Blue 2R 200	1·0	40·0	72·0	90·0	5·3	3·5	0·9
Durazol Fast Blue G 200 ...	1·0	75·0	87·0	95·0	1·8	0·9	0·6
Durazol Blue 2GN 200 ...	1·0	82·0	92·0	94·0	1·0	0·4	0·2
Durazol Fast Blue 4GS ...	2·0	33·0	65·0	86·5	8·0	2·5	1·3
Durazol Fast Blue 4R 200	0·5	35·0	73·0	92·5	4·5	1·0	0·4
Chlorazol Sky Blue FF 200	0·5	76·5	91·5	95·0	1·4	0·4	0·2
Chlorazol Sky Blue GW 400	0·5	50·2	84·0	94·5	1·7	0·5	0·3
Chlorazol Steel Blue 6B 150	1·0	—	—	—	—	—	—
Chlorazol Dark Green PL125	1·5	81·0	87·0	90·0	1·4	0·6	0·4
Chlorazol Green BN 125 ...	1·5	80·0	90·5	96·0	0·6	0·8	0·8
Chlorazol Green GS ...	1·5	75·0	88·0	92·0	0·7	0·6	0·4
Chlorazol Black BH 200 ...	1·0	82·0	91·5	96·0	0·7	0·4	0·2
Chlorazol Black EN 200 ...	2·0	74·0	80·0	83·0	1·4	0·9	0·7
Chlorazol Black E 200 ...	2·0	78·0	84·0	88·0	0·7	0·6	0·5
Chlorazol Black FF 200 ...	2·0	52·0	59·0	63·0	1·6	1·2	0·9
Chlorazol Black GF 200 ...	2·0	45·0	56·0	61·0	3·1	3·1	2·0
Chlorazol Black JH 200 ...	1·0	81·0	90·5	95·0	0·7	0·4	0·1
Chlorazol Black LF 150 ...	2·5	73·0	79·0	83·0	2·0	1·5	2·2
Chlorazol Black PB 150 ...	2·5	—	—	—	—	—	—
Durazol Grey N 150 ...	0·5	—	—	—	—	—	—
Durazol Grey RG 125 ...	1·0	62·0	79·0	88·5	0·3	0·2	0·2
Durazol Fast Grey B 125 ...	1·0	—	—	—	—	—	—
Durazol Fast Grey GS ...	1·5	75·0	84·0	90·5	1·3	0·4	0·4

L=60:1

@60:1
0
8%: 1.39/L
16%: 2.75/L

effect of ~~st~~ salt and t½ and E∞ @60:1 Vickerstaff 90°C

L=60:1	DYE% (%) dye	Eq 0% Na_2	8% Na_2	10% Na_2	t½ 0% Na_2	8% Na_2	10% Na_2
		E to			½-Rate		t½
Durazol Fast Yellow GR 200	0·5	34	65	77	4·2	1·8	1·7
Durazol Fast Yellow G 400	0·5	34	66	80	2·4	1·9	2·4
Durazol Fast Yellow 6GS ...	1·5	29	65	74	1·6	1·2	1·0
Chlorazol Yellow 6GS ...	1·0	14	28	37	1·6	3·2	4·1
Chrysophenine G 200 ...	0·5	9	29	38	0·6	0·8	1·0
Durazol Fast Orange 2G 125	1·0	6	32	47	1·6	1·8	2·0
Chlorazol Fast Orange D 125	1·5	5	22	36	—	—	—
Durazol Fast Orange 4R 150	0·5	13	46	62	4·0	3·4	3·8
Chlorazol Fast Orange R150	0·5	53	80	85	2·4	1·9	2·0
Chlorazol Orange PO 150 ...	0·5	30	57	68	1·7	1·6	1·7
Chlorazol Brown LF 150 ...	1·5	31	56	65	4·0	3·2	3·8
Chlorazol Brown M 150 ...	0·5	42	71	80	2·0	1·4	1·8
Durazol Fast Brown BR 150	0·75	39	81	87	—	—	—
Chlorazol Catechine B 125...	1·5	12	24	32	1·0	1·7	1·6
Chlorazol Catechine GR 150	1·5	24	36	44	—	2·2	1·6
Chlorazol Drab RH 125 ...	1·0	38	62	71	3·4	4·2	2·4
Chlorazol Orange Brown X 150	1·0	41	82	89	3·8	3·8	3·4
Chlorazol Orange Brown 2R 150	1.0	32	49	56	—	—	—
Durazol Fast Orange Brown 2RS	1·0	20	48	60	—	—	—
Chlorazol Bordeaux BS ...	1·0	39	71	85	2·8	2·0	1·9
Chlorazol Bordeaux 6B150	0·5	27	53	64	1·7	1·5	1·2
Chlorazol Fast Pink BF 200	0·5	0	16	28	—	1·4	1·4
Chlorazol Fast Red F 125...	1·0	26	46	59	2·4	1·4	2·0
Durazol Red 2B 150 ...	1·0	10	25	34	0·9	0·8	1·1
Chlorazol Fast Scarlet 4BAS	1·0	23	46	61	6·2	3·6	2·8
Chlorazol Fast Scarlet 4B 150	0·5	66	84	91	8·0	2·6	2·2
Chlorazol Fast Scarlet 8B 125	1·0	28	54	67	4·8	2·8	3·0
Chlorazol Fast Scarlet GS...	1·0	30	53	65	3·6	3·2	2·4
Durazol Fast Rubine B 150	1·0	12	29	43	—	5·2	2·8
Durazol Brilliant Red B 150	1·0	8	33	50	—	—	—
Durazol Fast Red 6BS ...	1·0	8	34	50	—	—	—
Durazol Fast Scarlet 2G 150	1·75	18	52	70	—	—	—
Durazol Helio B 200 ...	0·5	16	43	53	2·4	1·2	1·3
Chlorazol Fast Helio 2RK 200	0·5	18	48	58	1·4	1·0	0·9
Chlorazol Violet N 125 ...	0·5	32	73	84	4·6	2·0	2·8
Durazol Fast Violet 2BS ...	1·0	6	13	17	—	2·7	1·9
Chlorazol Blue B 200 ...	1·0	10	30	42	1·6	0·9	1·2
Chlorazol Blue G 150 ...	1·0	8	23	34	2·8	1·9	1·4
Durazol Fast Blue 3R 200	1·0	14	38	49	12·0	3·4	2·6
Durazol Fast Blue 2R 200	1·0	14	36	49	5·1	3·6	4·2
Durazol Fast Blue G 200 ...	1·0	15	35	49	2·6	3·6	4·1
Durazol Blue 2GN 200 ...	1·0	17	44	61	2·0	2·3	2·6
Durazol Fast Blue 4GS ...	2·0	4	27	39	—	—	6·0
Durazol Fast Blue 4R 200	0·5	6	34	54	—	2·8	2·8
Chlorazol Sky Blue FF 200	0·5	23	59	75	9·6	2·2	3·1
Chlorazol Sky Blue GW 400	0·5	4	48	64	4·8	2·6	1·7
Chlorazol Steel Blue 6B 150	1·0	5	56	72	4·4	2·0	1·8
Chlorazol Dark Green PL 125	1·5	34	58	66	1·7	2·6	2·7
Chlorazol Green BN 125 ...	1·5	56	78	86	4·4	5·9	4·0
Chlorazol Green GS ...	1·5	14	36	51	2·4	1·0	1·0
Chlorazol Black BH 200 ...	1·0	25	51	66	1·3	0·9	0·7
Chlorazol Black EN 200 ...	2·0	39	56	64	3·7	2·6	2·7
Chlorazol Black E 200 ...	2·0	33	53	62	3·0	2·8	2·2
Chlorazol Black FF 200 ...	2·0	25	41	50	1·6	2·0	2·0
Chlorazol Black GF 200 ...	2·0	19	48	62	1·2	2·6	3·3
Chlorazol Black JH 200 ...	1·0	24	49	65	3·9	1·9	1·8
Chlorazol Black LF 150 ...	2·5	34	54	63	6·8	3·7	3·4
Chlorazol Black PB 150 ...	2·5	23	47	58	3·2	3·1	2·8
Durazol Grey N 150 ...	0·5	45	68	72	1·4	1·6	1·7
Durazol Grey RG 125 ...	1·0	15	33	43	1·6	1·6	1·6
Durazol Fast Grey B 125 ...	1·0	12	33	47	2·6	5·6	3·3
Durazol Fast Grey GS ...	1·5	9	33	47	1·0	2·6	2·8
Durazol Fast Grey VGS ...	1·5	30	54	70	12·0	6·0	3·0
Chlorazol Diazo Black DB 150	2·5	20	37	48	—	—	—
Chlorazol Diazo Black 3B 150	2·5	21	37	48	—	—	—



Dyeing ~~Diffusion~~ Rate
Onset of Dye Aggregation (optical)
Salt Conc

Salt Sensitivity of Dyes

Effects: As salt concentration increases ...

liquor ratio

Equilibrium exhaust always increases

Diffusion coef may increase or decrease

If L is high (60:1), time of half dyeing ...
- decreases for 2/3 of dyes
- increases for 1/4 of dyes
- remains unchanged for 1/12 of dyes

If L is low (5:1) and salt conc is low,
- decreases for all dyes tested

Also:

Salt content of unpurified commercial dye is less important at high L (typically) ...
- @ 5:1, 1% dye contributes about 1.6 g/L salt
- @60:1, 1% dye contributes about 0.1 g/L salt

For purified dyes, results from 5:1 to 60:1 are predictable. For commercial dyes (containing salt and other diluents) results from 5:1 to 60:1 are not predictable.

SDC Classes

Class A

Class A in distinguished by leveling test using Direct Red 9 as standard

on wgt of goods

Leveling test/mock dyeing
1% dyed vs undyed yarn hanks
20% NaCl in mock dyebath
30:1 bath ratio
30 minutes
Boil
pH not specified

Class B/C

If not Class A (dye does not level as well as Direct Red 9), then further classify as B or C by salt sensitivity

1% dyeings with 3 g/L salt (1% owg)
use above conditions

continue dyeing same bath, new yarn

residual unexhausted dye in bath
raise salt conc to 60 g/L (20% owg)

If 1% salt original dyeing is darker than 20% run-on, then dye is Class B, else it's Class C

Direct Dyes

SDC Classification	C.I. Direct
A	Int. Yellow 2RLSW
B	Yellow 106
B	Orange 39
B	Red 89
B	Red 224
B	Red 243
B	Red 80
A	Red 9
B	Blue 90
B	Blue 80(s)
B	Blue 98(s)
B	Blue 80

Salt-Time Classes

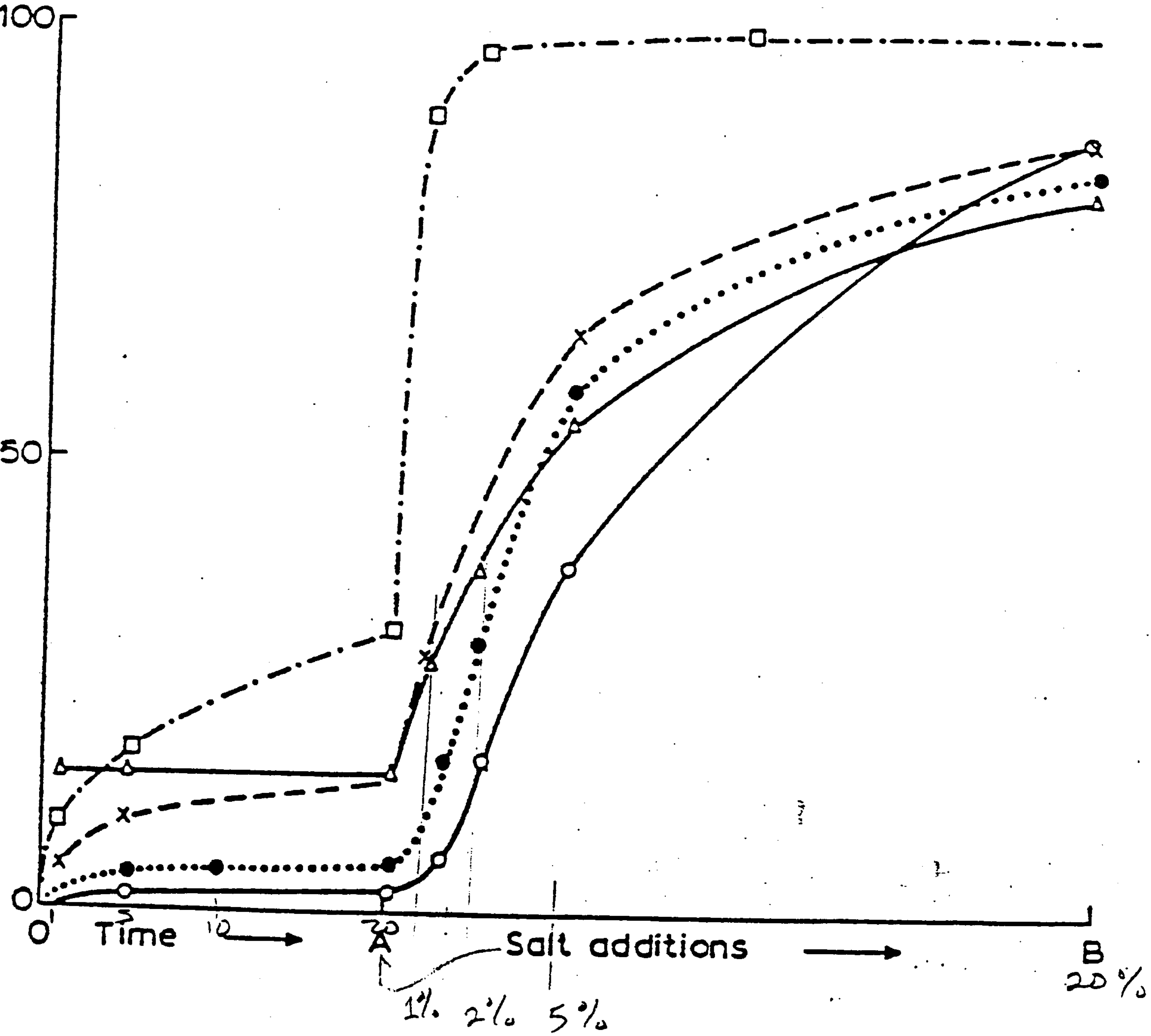
Boulton Classes: Takes *RATE* into account

Class I	**Dyes rapidly without salt to high equilibrium exhaustion**
Class II	**Dyes more slowly than I But good exhaust in 20 min**
Class III	**Requires salt for exhaust**

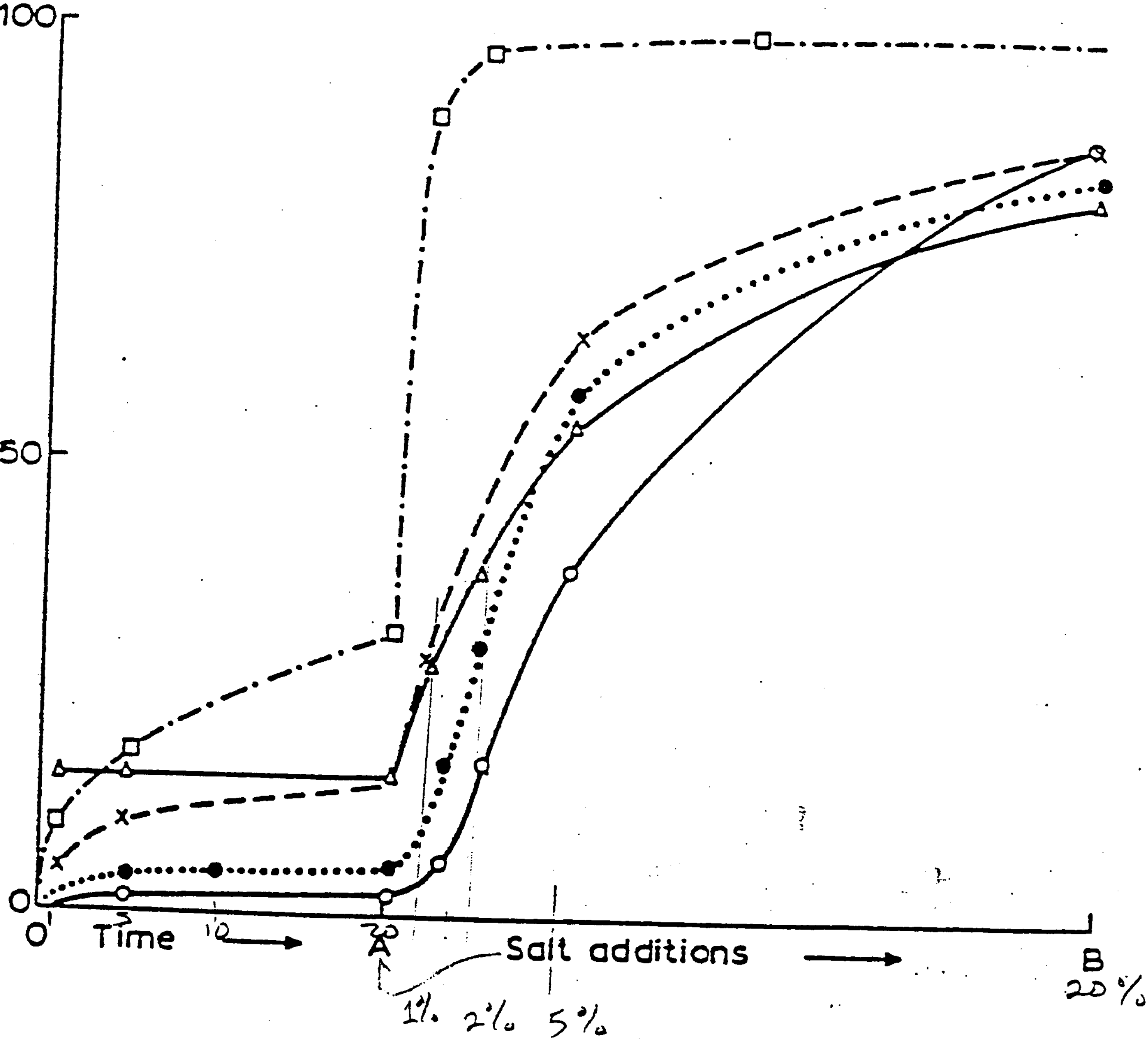
Within Classes I and II, there are "salt sensitive (SS) and non salt sensitive (NSS) dyes. All dyes in Class III are SS

<u>Procedure</u>

Dye 1, 5 and 20 minutes, 20:1 bath ratio, then add salt at 20 minute intervals: 1%, 2%, 5%, 20% owg. Remove skeins and evaluate color.



100
50
0
0
5
10
20
Time
A
Salt additions
B
1%
2%
5%
20%


100
50
0
0
5
Time
10
20
A
Salt additions
B
1%
2%
5%
20%

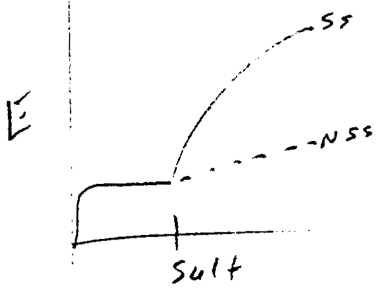
90°C, 20:1

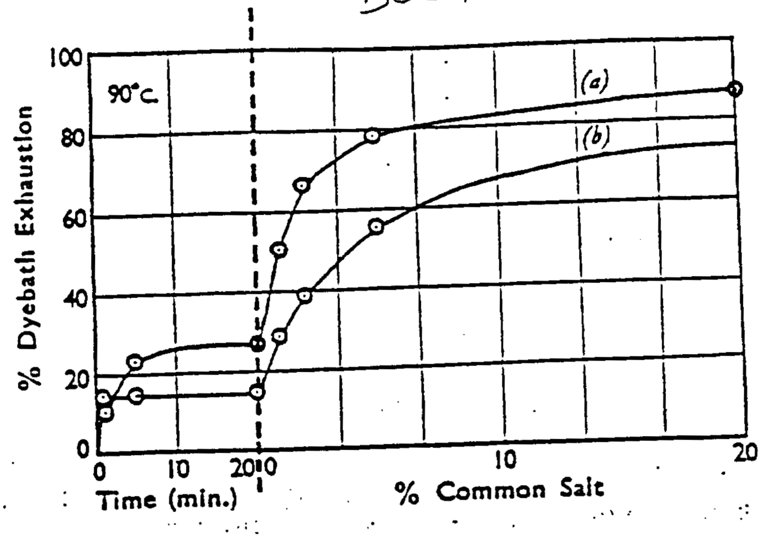
BOLTONS

Viscose

Tyr

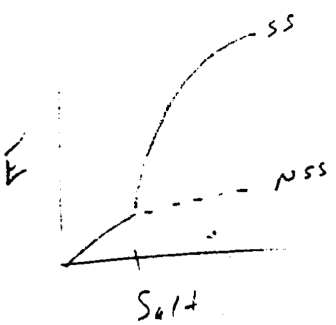
Typical

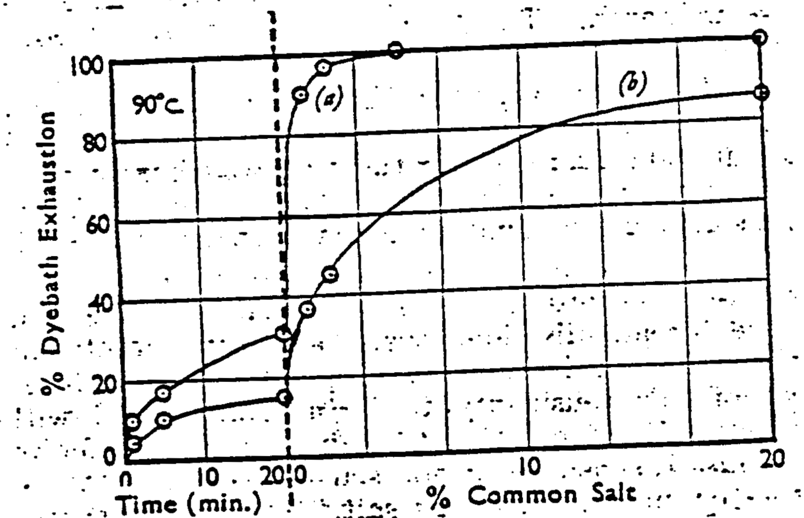




Time-Salt Test, Class I
(a) Chlorazol Fast Helio 2RKS
(b) Chlorazol Fast Orange GS

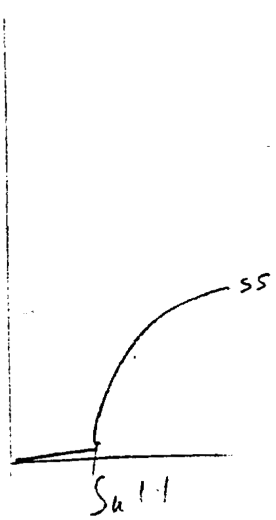
JSDC
1944
P8

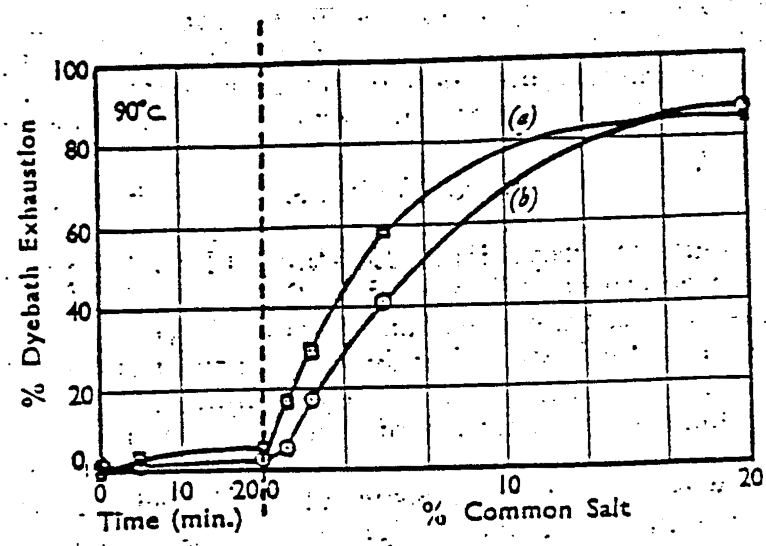




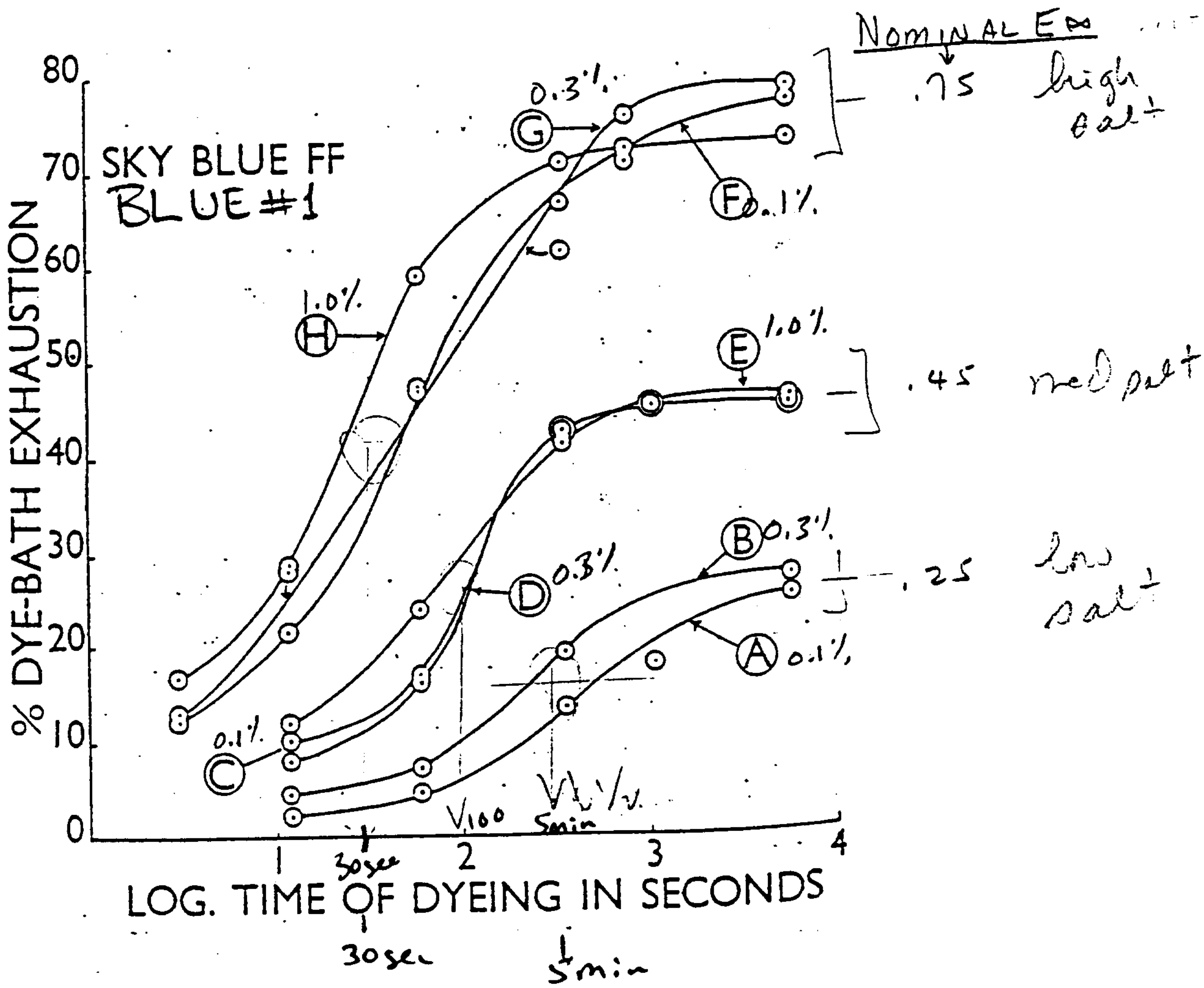
Time-Salt Test, Class II
(a) Benzopurpurine 4B Red 2
(b) Chlorazol Fast Red KS

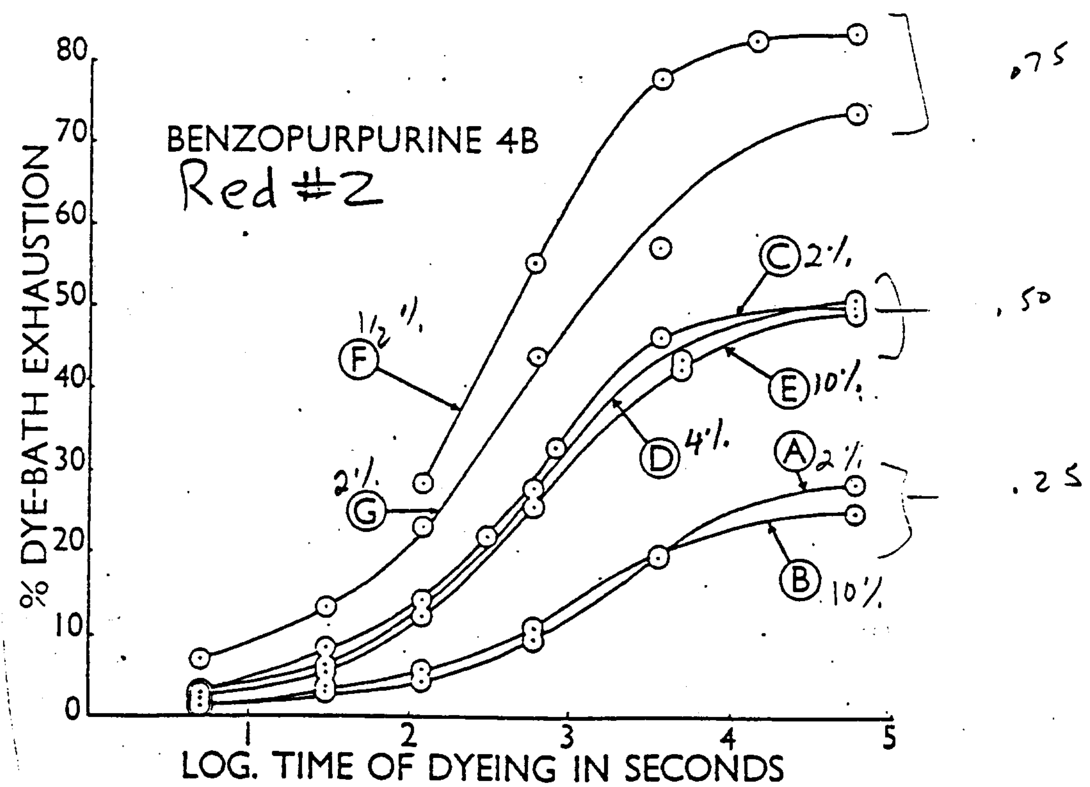
E



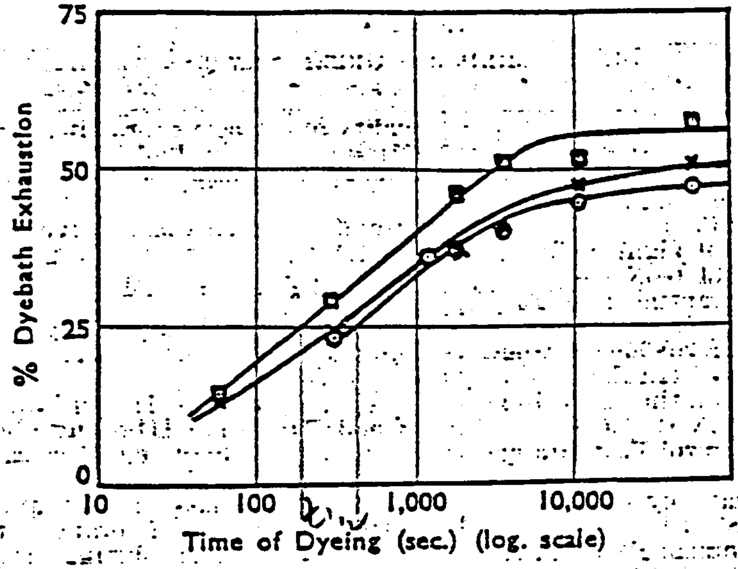


Time-Salt Test, Class III
(a) Chlorazol Fast Orange AGS
(b) Diphenyl Fast Blue-Green BL

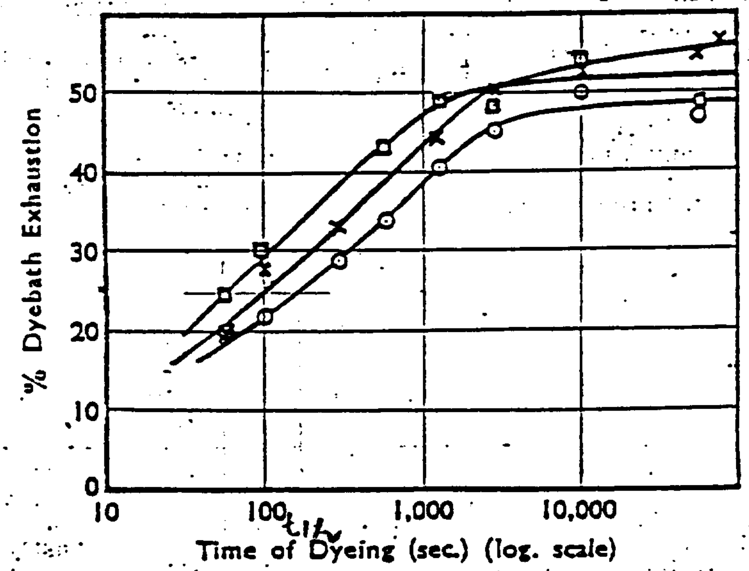

NOMINAL E∞
.75 high salt
.45 med salt
.25 low salt
SKY BLUE FF
BLUE #1
% DYE-BATH EXHAUSTION
LOG. TIME OF DYEING IN SECONDS
30sec
5min
V100
0.3%
0.1%
1.0%
0.3%
0.3%
0.1%
1.0%
0.1%


BENZOPURPURINE 4B
Red #2
% DYE-BATH EXHAUSTION
LOG. TIME OF DYEING IN SECONDS
.75
.50
.25
1/2 %
2%
2%
10%
4%
2%
10%

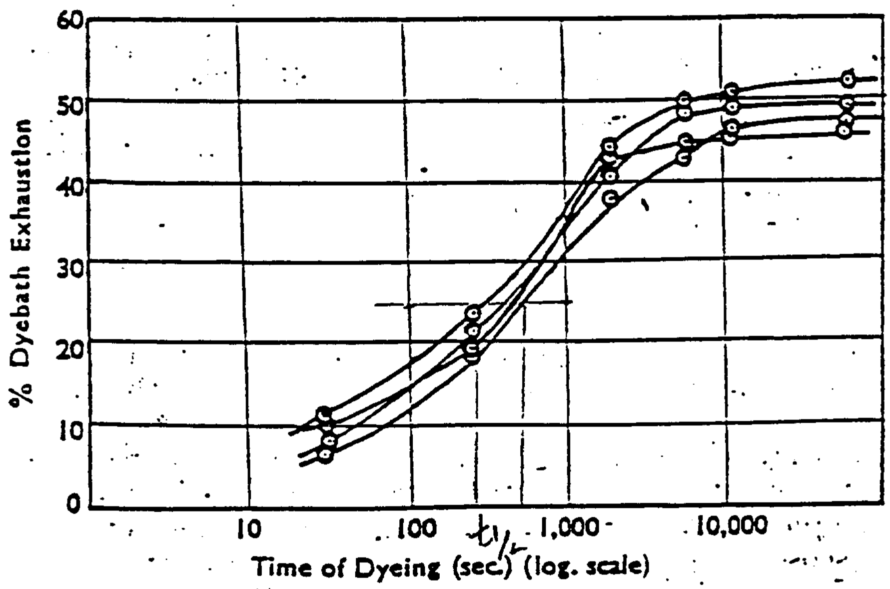
Different Depth of Shade for Same Dye



① Rigan Sky Blue G



② Chlorazol Fast Helio BKS



③ Benzo Fast Light Scarlet 4BL (purified)

Note: [illegible] Salt was used to give Em = .50

Rates of dyeing of direct dyes on viscose rayon   Peters III p44-48

Dye	Concentration of sodium chloride used (%)	Vickerstaff	Time of half-dyeing (min) Boulton
Chlorazol Fast Orange GS	5.0		0.07
Icyl Orange R OR 12	28.0		0.10
Diazo Brilliant Orange GR	4.0		0.22
Benzo Fast Yellow 4GL	8.5		0.26
Chrysophenine G (Y12)	13.0	0.3	0.26
Chlorazol Violet R Violet 3	5.0		0.50
Durazol Red 2B Red 81	5.0	0.5	0.84
Pyrazol Orange G	2.4		0.88
Primuline AS	2.0		1.00
Chlorazol Fast Yellow 5GKS	2.0		1.1
Benzo Fast Helio 4BL	5.4		1.2
Rosanthrene Pink	16.0		1.4
Benzo Fast Yellow RL	8.5		1.5
Chlorazol Dark Green PL GRN1	0.4	1.4	4.5
Benzopurpurine 4B Red 2	0.3		8.9
Oxyphenine GG	2.0		9.6
Chlorazol Fast Eosine B	7.0		7.0
Chlorazol Sky Blue FF Blue 1	2.0		15.9
Melantherine BH Blue 2	1.0		19.0
Chlorazol Brown MS	0.0		21.0
Trisulphon Brown B Brown 31	2.0		25.2
Chlorazol Green G Green 8	1.2	0.7	27.7
Benzopurpurine 10B Red 7	0.2		27.7
Diazo Black OT	1.0		42.8
Direct Fast Scarlet SE Red 23	0.0		100
Solar Orange 4G Or 60	10.0		126
Chlorazol Fast Orange AGS	3.3		156
Chlorantine Fast Scarlet BNLL Red 89	9.0		260

Dye @ 90°C 40:1 = L

exhaustion

⊛ Use enough salt to get E_∞ = 50% total, absolute (in other words $a^+ = a^s$)

Note $t_{1/2}$ ~ range of 2½ orders of magnitude

Note! Vickerstaff (JSDC, May 1946, p132) reported tests at 5:1 L & no salt to be ranging from 0.2 to 8 min. This was done w/no salt, thus lower affinity $-\Delta\mu^\circ \Downarrow \Rightarrow D\Uparrow, t_{1/2}\Downarrow$

Rates of dyeing of direct dyes on cotton

Dye	Time of half-dyeing (Boulton) (min)	5:1 Liquor ratio				60:1 Liquor ratio			
		No salt		3% salt		No salt		3% salt	
		Equilibrium exhaustion (%)	$t_{1/2}$ (min)	Equilibrium exhaustion (%)	$t_{1/2}$ (min)	Equilibrium exhaustion (%)	$t_{1/2}$ (min)	Equilibrium exhaustion (%)	$t_{1/2}$ (min)
Chlorazol Fast Helio 2RK200 Viol 7	0.18	61	0.3	91	0.2	18	1.4	58	0.9
Chrysophenine G200 Yell 12	0.26	39	0.3	82	0.2	9	0.6	28	1.0
Durazol Red 2B150 Red 81	0.84	41	0.5	83	0.2	10	0.9	34	1.1
Chlorazol Dark Green PL125 G1	4.5	81	1.4	90	0.4	34	1.7	66	2.7
Durazol Fast Blue 4R200	5.7	35	4.5	93	0.4	6		54	2.8
Chlorazol Violet N125	8.3	73	2.1	95	0.4	32	4.6	84	2.8
Chlorazol Blue G150 Blue 10	8.4	36	0.6	71	0.3	8	2.8	34	1.4
Chlorazol Sky Blue FF200 Blu 1	15.9	77	1.4	95	0.2	23	9.5	75	3.1
Chlorazol Steel Blue 6B150	18.3					5	4.4	72	1.8
Chlorazol Brown M150 BRN 2	21.0	89	0.8	98	0.1	42	2.8	80	1.8
Chlorazol Green GS Grn 8	27.7	75	0.7	92	0.4	14	2.4	51	1.0
Durazol Fast Violet 2BS	25.3	11	2.1	5.4	0.7	6		17	1.9
Chlorazol Fast Scarlet 8B125 R26	43.8	83	2.0	97	0.4	28	4.8	67	3.0
Chlorazol Black GF200 Blk 22	43.8	45	3.1	61	2.0	19	1.2	62	3.3
Chlorazol Drab RH125	115	77	1.0	91	0.4	38	3.4	71	2.4
Chlorazol Fast Orange AGS	156	52	1.6	82	0.4	6	1.6	47	2.0

purified dyes

Time

Process Considerations:

Dyeing Rate
Time/temp profile
Contact/stirring
Machine speed
Rate of heat/cool
Compatible combinations

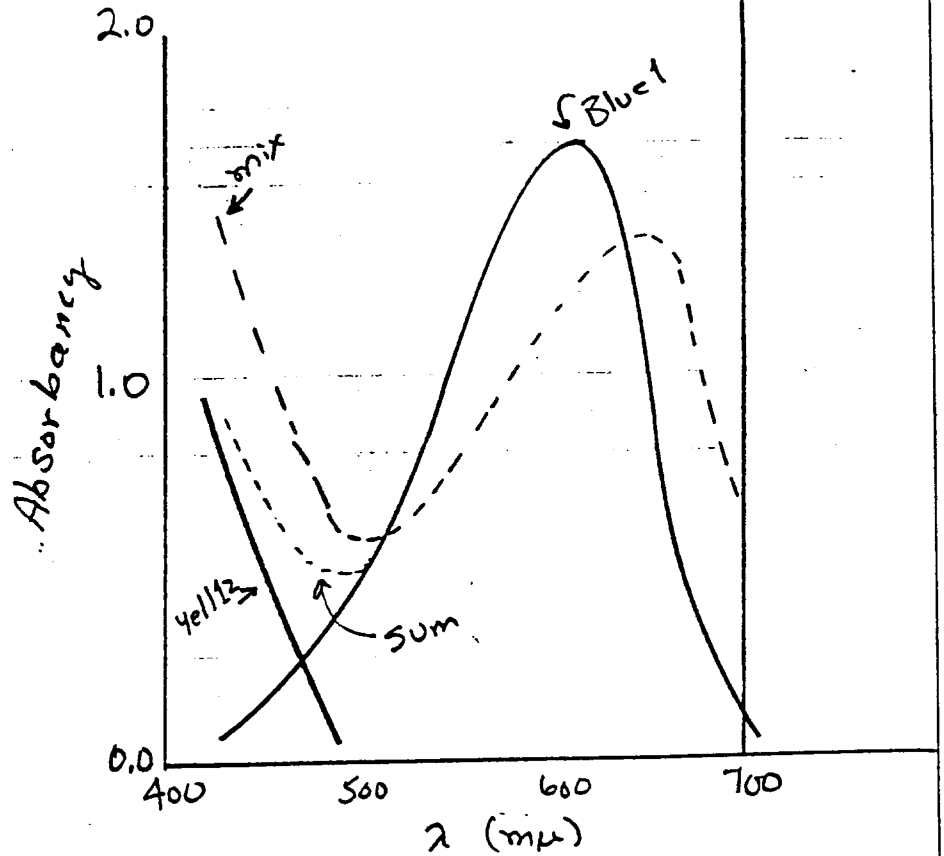
Mixtures

(1) Dyes in a mixture often behave differently than predicted from data on individual dyeing behavior. Following predictions are which dye will have the shortest half time of dyeing in 2 dye mix.

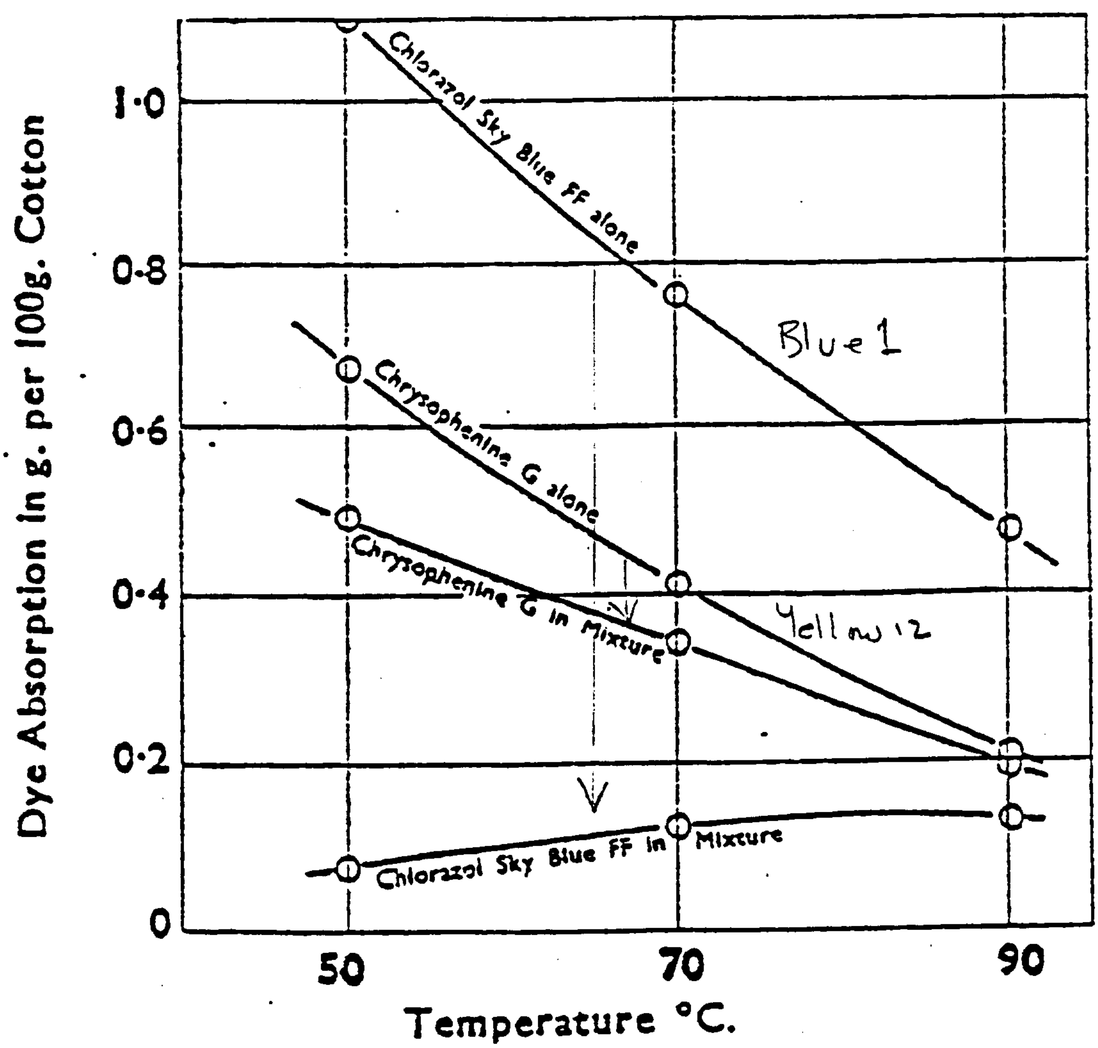
	SDC Cass		
	A	B	C
Prediction works	130	55	184
Borderline	33	31	64
Prediction fails	31	27	59
Total mixes tested	194	113	307

(2) We predict dye mixture behavior from optical measurements, as an indicator of interaction during dyeing.

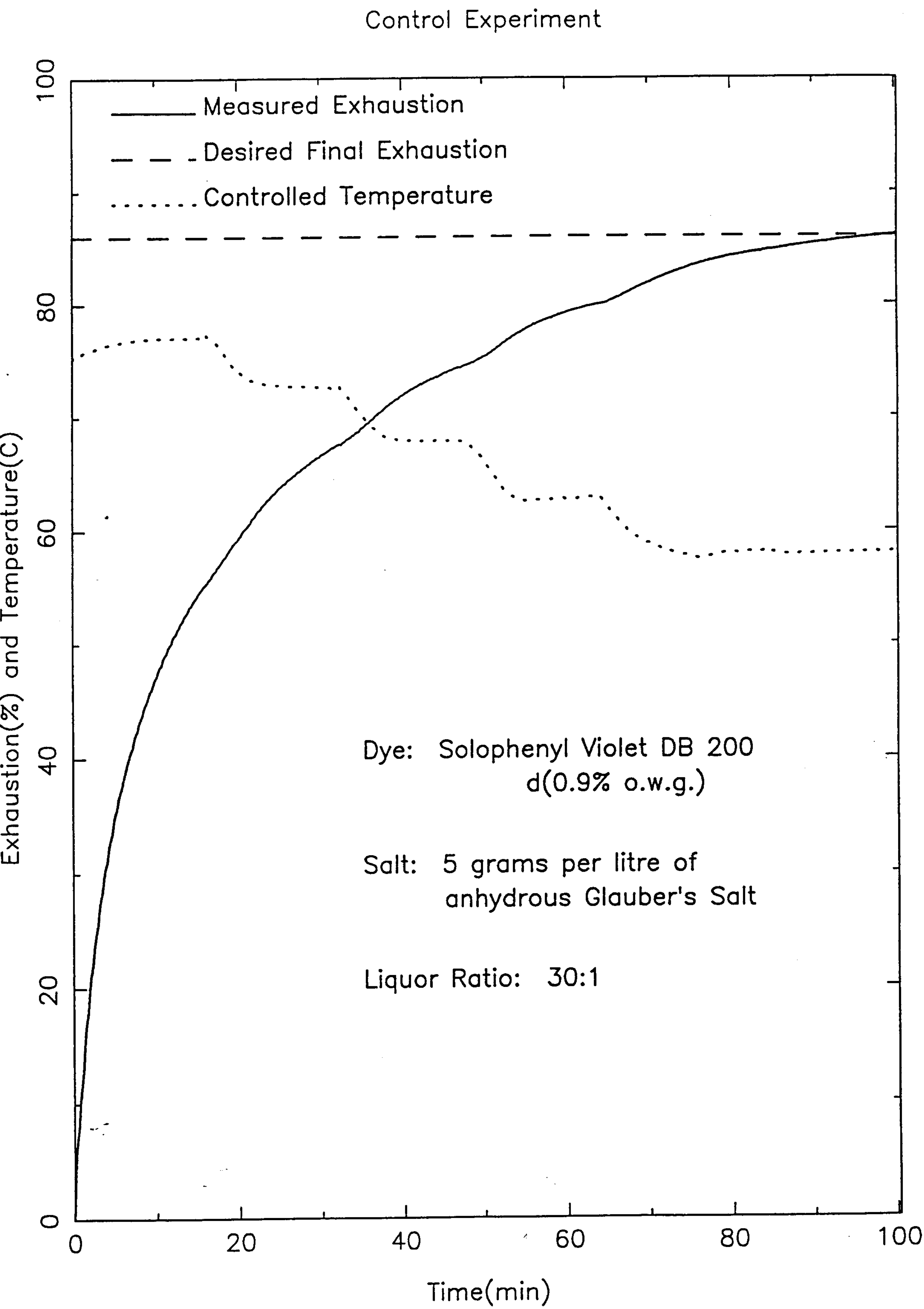
(3) All dye interactions in multi dye mixtures are predictable from 2 dye interactions

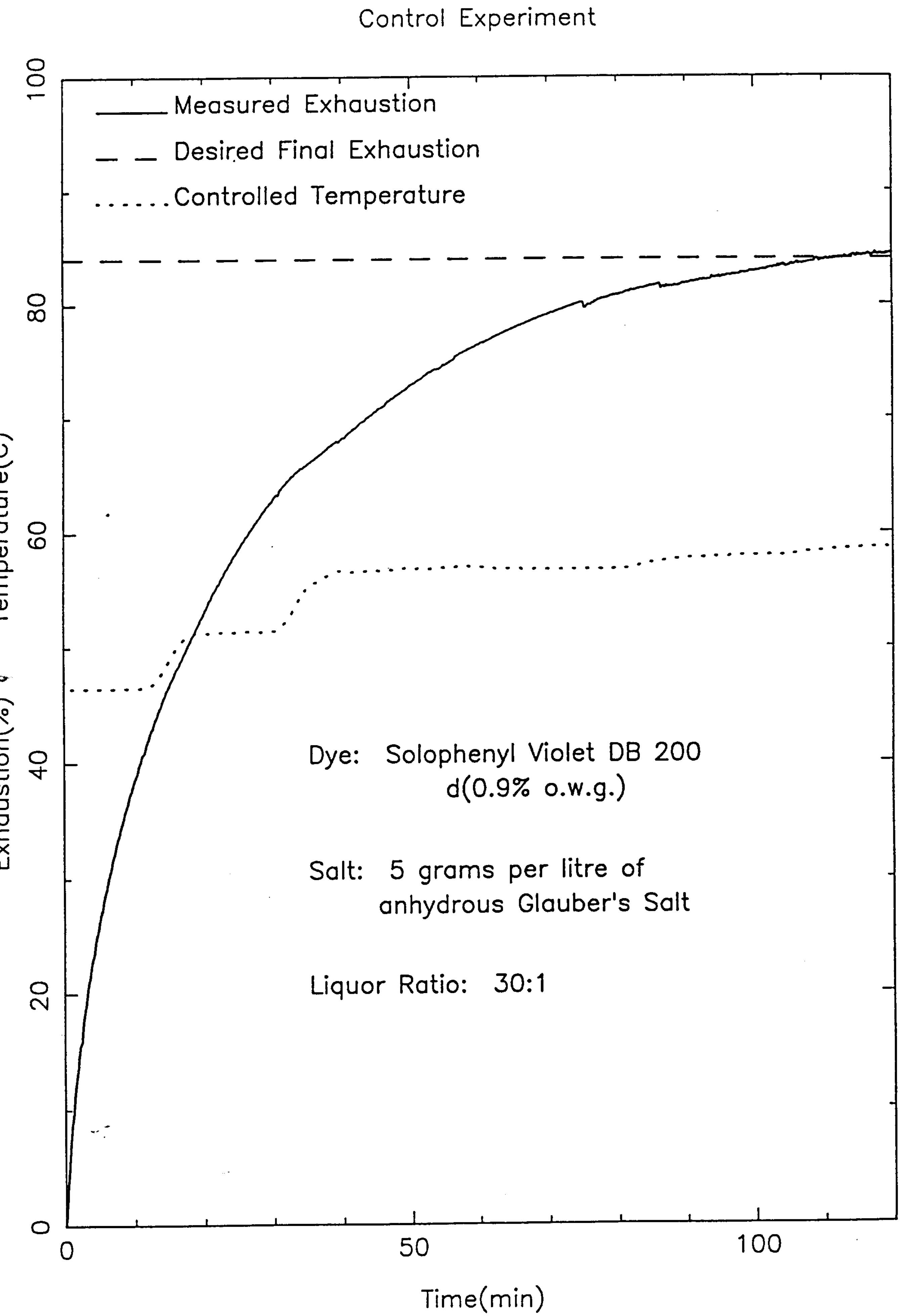


2.0
1.0
0.0
Absorbancy
mix
Blue 1
yellow 12
sum
400
500
600
700
λ (mμ)



Dye Absorption in g. per 100g. Cotton
1·0
0·8
0·6
0·4
0·2
0
Chlorazol Sky Blue FF alone
Blue 1
Chrysophenine G alone
Chrysophenine G in Mixture
Yellow 12
Chlorazol Sky Blue FF in Mixture
50
70
90
Temperature °C.


Control Experiment
Measured Exhaustion
Desired Final Exhaustion
Controlled Temperature
Dye: Solophenyl Violet DB 200
d(0.9% o.w.g.)
Salt: 5 grams per litre of
anhydrous Glauber's Salt
Liquor Ratio: 30:1
Exhaustion(%) and Temperature(C)
Time(min)
0
20
40
60
80
100


Control Experiment
Measured Exhaustion
Desired Final Exhaustion
Controlled Temperature
Dye: Solophenyl Violet DB 200
d(0.9% o.w.g.)
Salt: 5 grams per litre of
anhydrous Glauber's Salt
Liquor Ratio: 30:1
Time(min)
0
50
100
20
40
60
80

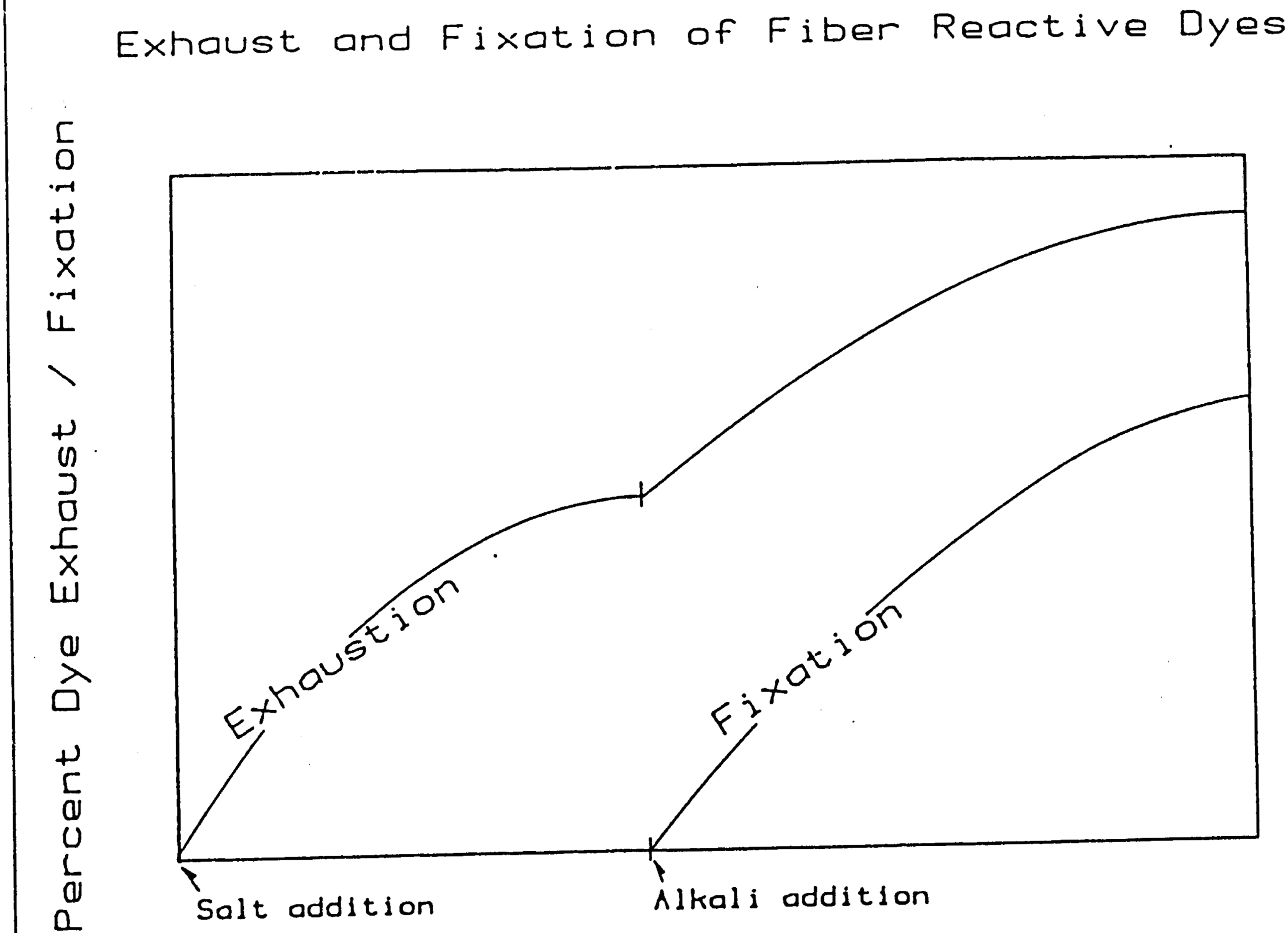
Fiber Reactive Dyeing

Fiber Reactive Dyeing Methods

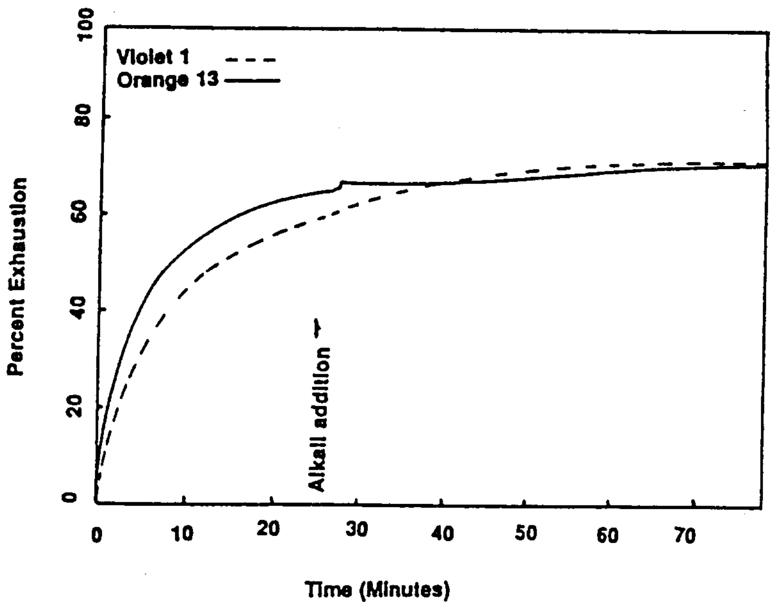
	Conventional	*Constant temperature*	*High temperature*	*All-In*
1.	Set bath and load substrate	Set bath and load substrate	Set bath and load substrate	Set bath and load substrate
2.	Add dye	Add dye	Add dye	Add dye
3.	Run	Run	Run	Run
4.	Add salt	Heat to dyeing temperature*	Heat to high temperature*	Add salt
5.	Heat to dyeing temperature (*)	Add salt	Cool to dyeing temperature *	Heat to dyeing temperature*
6.	Add alkali	Run for exhaust	Add salt	Run for exhaust and reaction
7.	Run for reaction	Add alkali	Run for exhaust	Cool
8.	Cool	Run for reaction	Add alkali	Wash
9.	Wash	Cool	Run for fixation	Apply fixative
10.	Apply fixative	Wash	Cool	—
11.	—	Apply fixative	Wash	—
12.	—	—	Apply fixative	—

*Typical dyeing temperatures are 175°F for hot types, 140°F for cold
**High temperatures are 203°F for hot types, 160° for cold

Figure 2

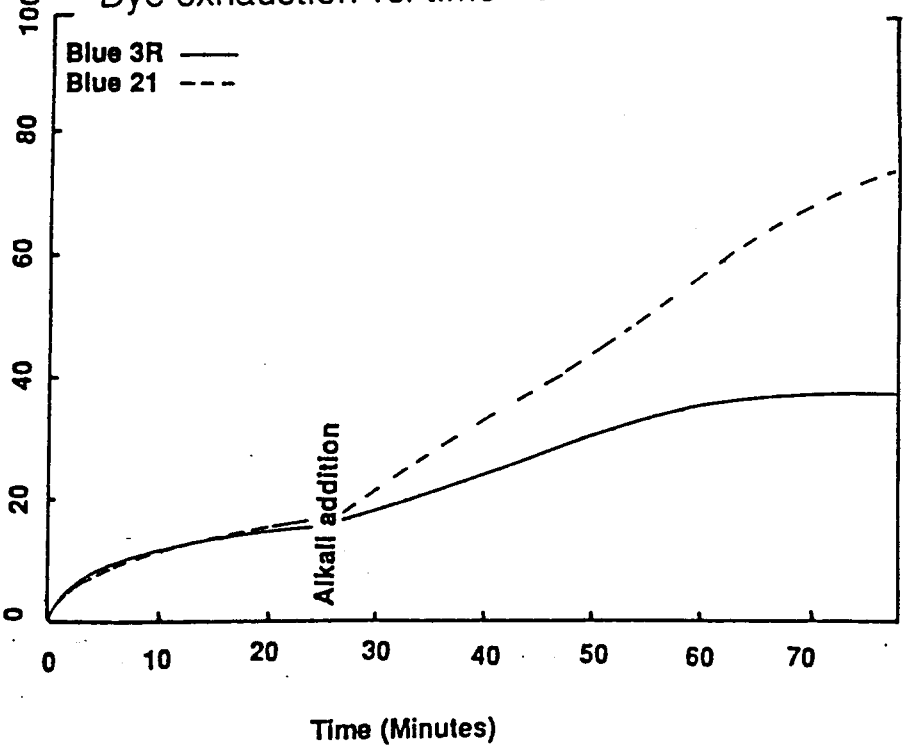

Exhaust and Fixation of Fiber Reactive Dyes
Percent Dye Exhaust / Fixation
Exhaustion
Fixation
Salt addition
Alkali addition

Dye exhaustion vs. time—Violet 1 and Orange 13.



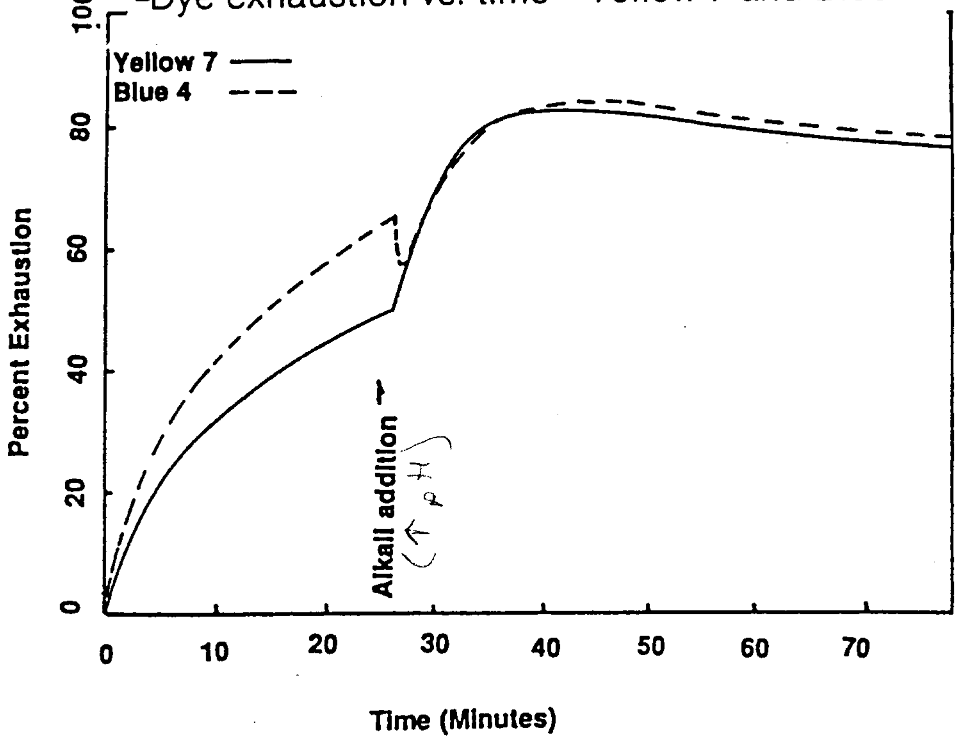
Typical Triazine

-Dye exhaustion vs. time—Blue 3R and Blue 21.

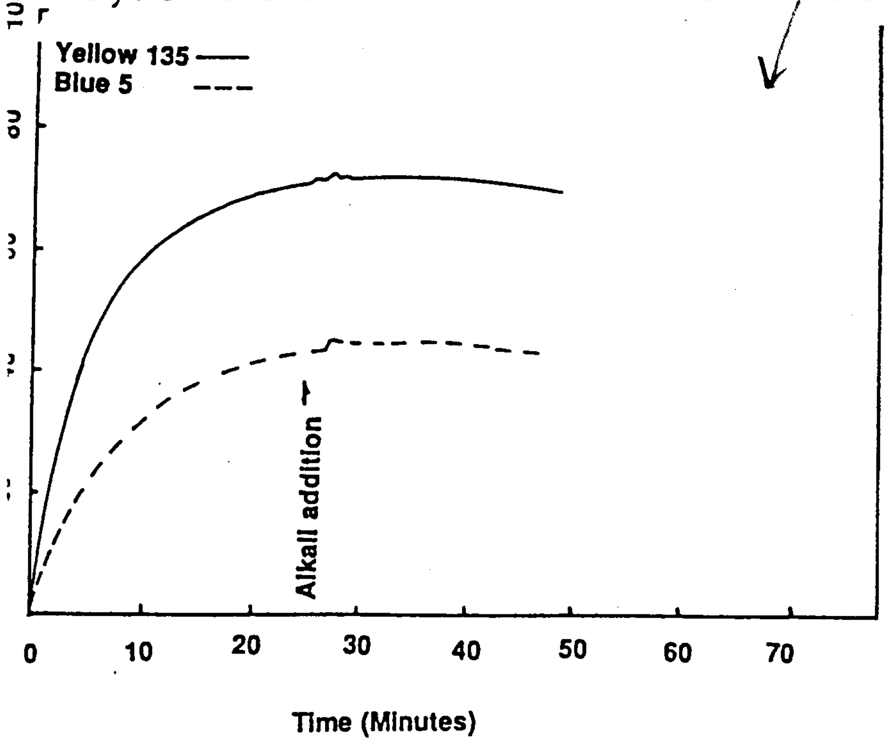


Typical Vinyl Sulfone

-Dye exhaustion vs. time—Yellow 7 and Blue 4.



-Dye exhaustion vs. time—Yellow 135 and Blue 5.



-Dye exhaustion vs. time—Blue 19 and Red 180.