Interference Coloring for Architectural & Special Applications

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Electrolytic coloring processes capable of achieving a vast number of new colors ranging from grey, to blue, green, yellow, and violet have been available for many years. The various possibilities of producing these colors are examined, and the proprietary interference coloring process is explained, with experimental data from industrial production plants provided. This process is applicable for standard architectural materials, and for some other special applications as well (such as aerospace and hard anodizing).

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[*]An Introduction

The anodic oxide that forms on aluminum and its alloys during the electrolytic process has a porous structure that can be colored by absorption or by the electrolytic process (1-3).

The former method, using azoic colorants very similar to those used to dye fabrics, achieves a vast range of colors, but unfortunately, the light fastness of most is insufficient to allow for outdoor exposure.

Electrolytic colorings possess all the quality requisites needed for the use of anodized aluminum for architectural purposes; however, the color range, from bronze to black, is very limited. There have been many attempts to widen this range, but interesting results were only obtained after the introduction of colorings by *Interference* (4-18).

The *Interference* procedure can be outlined in the following way:

1. Conventional anodizing in sulfuric acid.
2. Modification of the bottom of the pore; e.g. in a 10 g/l solution of phosphoric acid, 10V alternate current for a few minutes.
3. Electrolytic coloring, usually in a nickel salt based solution achieving colors ranging from blue to green, through yellow and violet, with a marked tendency (at least in relation to the first technologies) towards an iridescent effect.

The way coloring by interference operates was clearly explained by P.G. Sheasby et al. (4, 17) who were able to observe that the bottom of the pore becomes *enlarged* during the phosphoric acid treatment and the modification appears to be responsible for the *interference* effect.

Procedures have more recently designed where the bottom of the pore is modified in weak acid solutions with the possible addition of metal salts.

One of the current technologies (18) involves pore modification and the subsequent coloring phase in a nickel and/or tin salt based slightly acid solution. In these conditions, following the application of a complex alternate current at low voltage, it is possible to modify the crystalline structure of the barrier layer caused by the phenomenon known as *recovery effect.*
This modification of the barrier layer is able to condition the following coloring phase, theoretically producing all the colors of the visible spectrum. A fundamental part of this technology is the power supplier that must be able to supply alternate current of appropriate characteristics.

The New Technologies

Special coloring processes have recently been developed* for the grey tones and for a wide range of pastel shades (colors of the visible spectrum).

With the process, great results have been obtained: **equipment and techniques go far beyond the traditional "bronze type" coloring.**

The technology (*Figure 1*) consists of the following phases:

1. Conventional anodizing with anodic thicknesses as established by international standards for architectural use.
2. Modification treatment in a low concentrated sulfuric acid solution with a special additive able to protect the aluminum oxide layer and facilitate the modification process. The treatment is accomplished by electrolytic process with a special alternate current generated by a specially designed power supplier. In addition, a specially designed computer controls the low voltage alternate current at particular frequencies.
3. Electrolytic coloring in a conventional tin based solution.
4. Pore sealing with one of the conventional methods, either hydration or impregnation.

The obtained colors have optimum light fastness properties and a behaviour to exposure similar to that of conventional *two-step electrocoloring*.

[1]Tests in Kesternich's chamber, according to DIN 50 018, did not, in fact, give rise to changes in aspect. Moreover, the simulated exposure test (*artificial weathering*) according to standard DIN 53 384 gave a *no color change* result. The performance results above are logical because

[*] GREYLOX & MULTICOLOR, Italtecno, S.r.l., Modena, Italy

[1] Tecnocdor Rectifier, Italtecno S.r.l., Modena, Italy

the coloring treatment is essentially the same as that of conventional two-step electrocoloring, since both systems deposit tin particles within the pores.
The actual color differences are created by the different *orientation* assumed by the particles, which is caused by the alterations to which the barrier layer is subjected during the *modification* phase.

Laboratory tests (21) have shown that the obtainable colors do not depend on the time length of the final phase, the tin salt bath. The colors depend specifically on the parameters (time, type, and quality of current) in use during the modification phase.

Significant variations to the tin salt coloring phase (1 to 2 minutes longer, 1 to 2 volts stronger) have not lead to important differences or any change in the *obtained* colors, but merely slight differences in tone.

Abrasion according to the *Taber* test method was carried out to confirm that the quality of the oxide layer was not altered by immersion in the acid solution during the modification process.

Comparisons between natural (non-colored) layers, *two-step* bronze electrocolored layers, and three standard proprietary process layers were produced, and are given on *Table 1* and *Graph 1.*

The Process

Step One: The Anodizing Step

Sulfuric acid	160 - 220 g/l *
Aluminum (dissolved)	7 - 10 g/l **
Temperature	68 °F (± 1.0°) ***
Current density	15 A/ft^2
Anodic thickness	>10 microns

* It is possible to choose a standard H_2SO_4 concentration between the suggested range but it is necessary to maintain the H_2SO_4 concentration in a very narrow range (± 3 g/l).

** Dissolved aluminium level is important and should be controlled.

*** Temperature control is critical, use of appropriate chillers and heat exchangers is necessary.

Step Two: The Modification Step

Sulfuric acid	30 g/l *
Color Additive	40 g/l **
Temperature	66 °F (± 0.5°) ***
Current density	5 A/ft^2
Treatment Time	10 - 15 min. ****

* Concentration control is critical.
It is necessary to maintain the concentration within a very narrow range. A particular patented computerized power supplier is necessary.

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*** Temperature control is critical.
The use of appropriate chillers and heat exchangers is necessary.

**** Depends on the color shade required and anodic layer characteristics.

Step Three: The Electrocoloring Step

The different colors can be achieved by electrocoloring in a standard tin-based solution for 1-5 minutes.

A patented computerized power supplier, [1] specifically designed for the process, is required. This power supplier can be used for step two and step three of the process.

Step Four: The Sealing Step

The processed profiles may be sealed in conventional high temperature, medium temperature and low temperature (cold) sealing processes.

The Performance Tests Passed

Tests for Oxide Quality

ISO 1463	No ASTM Test
ISO 2106	ASTM B-137
ISO 2360	ASTM B-244

Tests for Sealing Quality

ISO 2143	ASTM B-136

ISO 2931	ASTM B-457
ISO 2932	No ASTM Test
ISO 3210	ASTM B-680

Tests for Corrosion and Light Resistance

Resistance to Kesternich Test

Method:	DIN 50 018 SFW 0.2 S
Duration of test:	5 and 10 cycles of 24 hrs.

Resistance to Artificial Weathering & UV Light

Method:	following DIN 53 384
Duration of test:	2400 hrs.
Apparatus:	QUV spray option apparatus
Light source:	8 fluorescent the UV-A 340 lamps with a spectrum from 295-400 nm. The lamps have a peak emission at 340 nm. Below 300 nm, emission is less than 2% of its total light output.
Test conditions:	5 hrs. Dry UV exposure with a black standard temperature of 122°F ± 2°F, relative humidity 10% ± 5%, followed by 1 hr. conditioned water spray, without radiation at 68°F ± 2°F black standard temperature.

Florida Test

Taber Test

The Modification Requirements

Modification Power Supplier

A special transformer is required for the modification step (20-21). A polyfunctional power supplier able to deliver:

- Direct Current
- Conventional Alternate Current
- Alternate Current at Variable Frequencies
- A Combination of Direct and Alternate Current at Variable Frequencies

A specially equipped and patented power supplier has been designed and manufactured to meet these requirements. The rectifier and transformer is a fully computerized, 3 phase, with changeable frequency rectifier.

Size of the rectifier is determined by the following:

“A ” x 5 = Total Amperage

where

“A” is ft^2 of the biggest load to be colored.

Computerized Modification Control

Control of all these parameters obviously is of extreme importance. A specially designed Anodizing Process Computer (*APC)* is included with the rectifier for this purpose. The computer executes upto 100 programs and can be connected to a main computer for statistical process control.

Modification Electrode Type and Design

Stainless steel AISI 316 L is recommended.

Modification Thermo-Regulation

The process requires that the thermo-regulation of the modification tank be optimal at a ± 0.5° F variation of temperature. Therefore the tank must be equipped with heating (e.g. by means [*]of heating serpentine) and cooling capability (e.g. heat exchanger).

It is also necessary to utilize a system that allows for greater uniformity of the solution (by means of air blowing distributed in the tank using Venturi diffusers and circulation pumps).

The heat that develops during the modification step is limited; however, variations in bath temperature, especially as related to environmental factors, greatly effect color consistency. Therefore, the thermo-regulation in the modification step must be designed to consistently limit temperature variation. The better the consistency of temperature control the better the color consistency.

[*] MicroBubbles, Italtecno S.r.l., Modena, Italy

The use of air blowing is recommended to guarantee a homogeneous mixture of the electrolyte, after the addition of the chemicals, and an uniform temperature of the solution. The system utilizes a specially designed, patented diffuser system.*

The Electrocoloring Requirements

Existing Transformer, Tank and Solution (Option A)

It is possible to use an existing transformer for the electrocoloring step if the transformer exhibits very good performance in standard electrocoloring. In particular the existing transformer, tank and solution must have very good throwing power, very good color uniformity, and very good color reproducibility.

Note: the existing transformer can not be used for the modification step.

Parallel Connection Between The Modification Tank And Electrocoloring Tank (Option B)

It is also possible to make a parallel connection between the *Tecnocolor* transformer used for the modification tank and the electrocoloring tank.

Note: in this way it is possible to use only one transformer but it is not possible to use the two tanks simultaneously.

Electrocoloring Thermo-Regulation

The electrocoloring step requires a good thermo-regulation of the tank. It is possible to work at the preferred temperature of the customer, but that temperature must be kept in a maximum variation of ± 2 °F.

The Evaluation of Colors

The usual method of evaluating and adjusting colors is generally empirical and depends on the practical experience of the operator. It is therefore generally impossible to have an objective reference.

However, to help the anodizer evaluate the obtained colors, we accurately researched instrumental evaluation techniques as the parameters applied during the *modification* phase varied (i.e. applied voltage verses color code and treatment time). Measurements were made with an *X-Rite Spectroscope*. Interestingly, this instrument excludes the finishing effect (polished verses etched) and gives an objective value that can be correlated over time. The data obtained from that research are given in *Tables 2-4* and *Graphs 2-4*.

By following the suggested voltage and time trends, operators can obtain desired colors. An operational table is produced for each customer based on the customer's specific requirements and operational parameters.

Conclusions

A new technology for producing high performance electrolytically colored anodized aluminum has been described.

The new technology, produces attractive colors that are excellent for outdoor purpose; respective of current corrosion, abrasion resistance, and color fastness common to general industrial standards and requirements.

The process is suitable both for decorative and architectural application and opens new markets to the aluminum industry.

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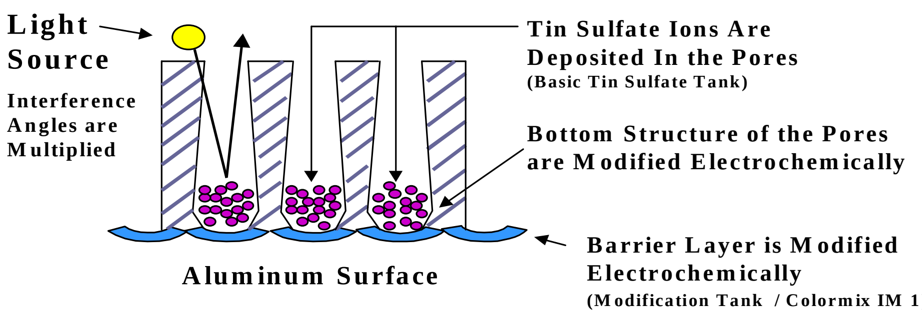
Figure 1



- ***Colors Are Derived by "Optical Interference"***
- ***A Vast Range of Electrolytic, High Performance Colors are Produced With Near 100% Repeatability***

Grey	***Blue***	***Turquoise***	***Purple***	***Violet***
Green	***Yellow***	***Orange***	***Emerald Green***	

Table 1

Taber Test Results						
Color	1000 rounds	2000 rounds	3000 rounds	4000 rounds	5000 rounds	6000 rounds
Natural	3.60	5.40	8.70	11.20	16.70	21.70
Bronze	3.10	5.80	8.20	10.60	15.00	20.70
Black	3.10	5.80	9.70	12.20	18.10	25.20
Grey	4.00	6.30	9.80	13.30	18.70	24.60
Blue	2.50	5.70	8.00	11.40	17.20	23.80
Green	3.60	6.60	9.60	12.60	18.00	23.30

Note: The behaviour of the different colors is similar and it is possible to consider the process similar to a standard electrocolouring treatment.

Graph 1

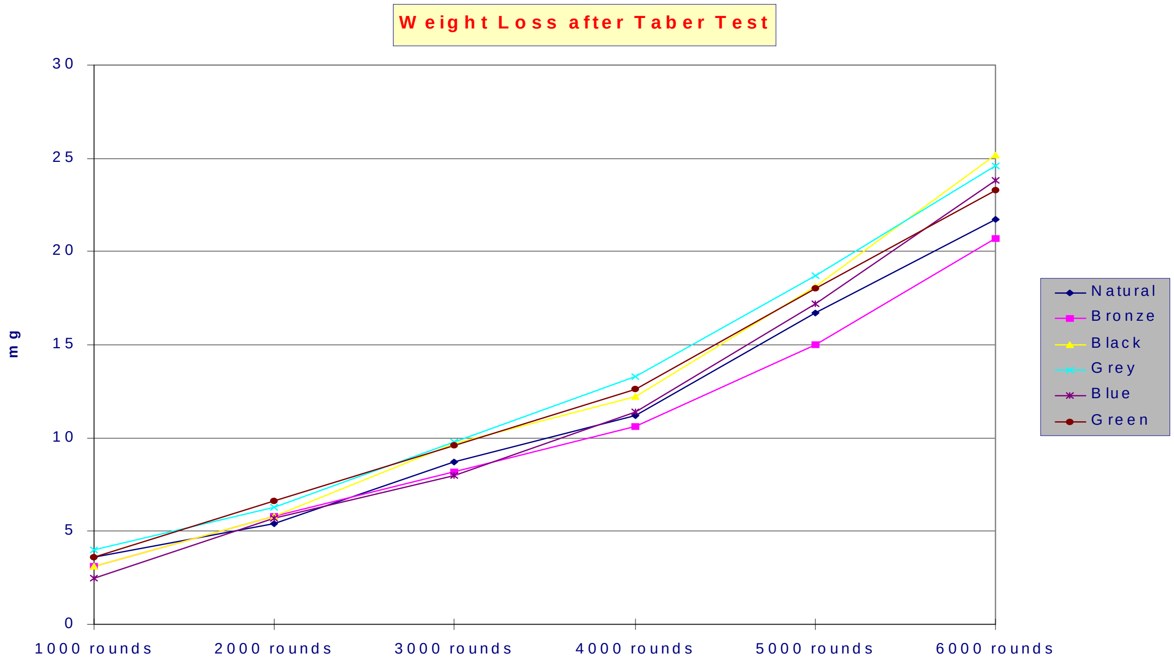


Table 2

Volt	Code / Col. par.	2.10	2.20	2.30	2.40	2.50	2.60	2.70	2.80	2.90	3.00
2.50	L	34.59	32.73	32.15	33.32	33.77	37.00	38.84	42.35	45.95	47.41
	a	3.92	4.53	2.14	0.14	-2.15	-3.55	-5.38	-7.58	-9.77	-9.94
	b	3.49	-1.68	-8.00	-12.49	-14.51	-14.85	-14.29	-11.88	-8.26	-5.72
	t(m,sec)	20.00	20.14	20.35	20.55	21.10	21.20	21.35	21.50	22.05	22.22
	Colour	bronze	bronze/violet	violet	violet/blue	blue	sea blue	sea blue	sky blue	blue/green	green
3.00	L	27.24	37.83	40.73	41.71	44.46	44.69	47.02	48.43	52.04	53.40
	a	2.73	0.60	-0.44	-2.71	-4.49	-5.90	-7.96	-8.85	-9.86	-10.10
	b	-5.14	-9.50	-10.90	-12.33	12.27	-10.40	-6.51	-3.97	2.42	5.72
	t(m,sec)	16.01	16.16	16.30	16.48	17.03	17.12	17.25	17.46	18.02	18.16
	Colour	violet	violet/blue	blue/violet	blue	blue	blue	blue/green	blue/green	green	green
3.50	L	36.41	42.10	46.32	49.90	50.58	52.52	53.37	55.79	56.40	57.85
	a	2.21	1.07	-1.35	-3.14	-5.11	-6.58	-7.72	-7.93	-8.96	-8.64
	b	-4.85	-7.60	-7.20	-7.95	-6.42	-4.51	-1.21	0.64	6.52	11.05
	t(m,sec)	13.35	13.54	14.07	14.27	14.38	14.56	15.13	15.23	15.35	15.49
	Colour	violet/grey	violet/grey	grey/pail blue	grey/pail blue	grey/pail blue	green/blue	green/blue	green	green	green
4.00	L	42.52	43.03	46.10	47.67	50.07	51.96	52.60	54.04	55.91	55.44
	a	-0.46	-2.76	-3.53	-12.20	-6.32	-5.91	-6.53	-7.23	-7.11	-6.47
	b	0.12	0.95	0.01	0.81	2.31	1.37	3.62	7.27	11.24	15.39
	t(m,sec)	12.20	12.31	12.43	12.52	13.03	13.12	13.22	13.35	13.51	14.05
	Colour	grey	grey/pail blue	grey/green	grey/green	green	green	green	green	green	green/yellow
4.40	L	48.82	49.10	50.59	50.39	49.60	52.43	51.48	55.78	55.61	57.15
	a	0.29	-1.32	-2.97	-3.83	-4.88	-6.49	-6.42	-6.31	-5.87	-5.72
	b	1.83	1.31	0.62	0.28	3.58	3.90	8.85	9.99	13.58	15.89
	t(m,sec)	11.22	11.33	11.44	11.56	12.07	12.16	12.30	12.39	12.54	13.01
	Colour	grey/bronze	grey	grey/green	grey/green	green	green	green	green	green	green
4.80	L	50.01	50.41	51.46	50.11	50.46	52.04	51.98	53.06	53.16	55.64
	a	0.27	-0.87	-1.75	-2.44	-3.58	-3.75	-4.14	-4.68	-4.37	-4.65
	b	6.17	5.17	3.87	4.57	5.69	6.35	9.13	11.78	14.01	14.09
	t(m,sec)	10.40	10.50	11.03	11.13	11.29	11.36	11.50	12.03	12.13	12.25
	Colour	grey/green	grey/green	grey/green	grey/green	green	green	green	green	green	green

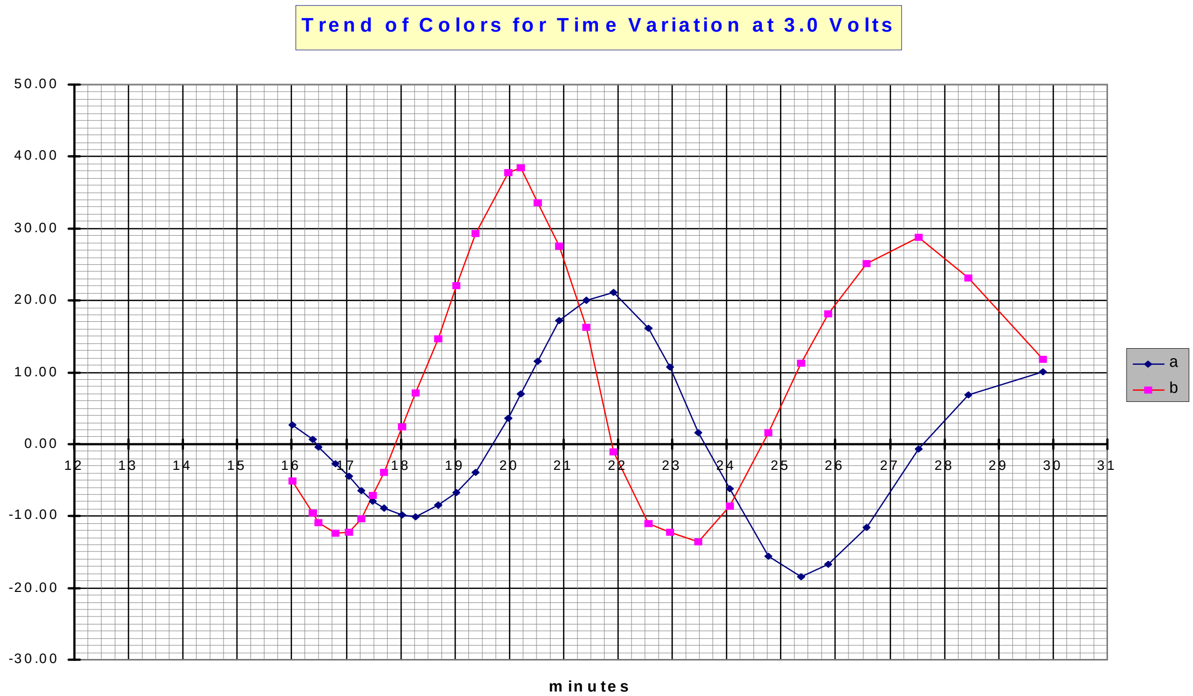
Table 3

Volt	Code / Col. par.	3.15	3.30	3.45	3.60	3.75	3.90	4.00	4.20	4.40	4.60	4.80	5.00
2.50	L	50.98	52.99	53.20	54.62	52.79	51.85	49.05	44.25	40.48	36.20	32.93	30.69
	a	-11.05	-11.77	-10.45	-5.44	-0.98	2.58	3.50	12.66	17.24	19.73	20.88	5.90
	b	2.36	6.62	14.93	24.73	31.40	34.78	31.89	30.84	18.85	6.57	-2.54	-15.15
	t(m,sec)	22.47	23.30	23.51	24.12	24.40	25.00	25.15	25.55	26.20	26.57	27.25	28.05
	Colour	green	green	green/ye	yellow/gr	yellow	yellow	yellow	orange	ange/purp	purple	purple	violet
3.00	L	54.01	55.24	53.51	52.64	50.32	48.26	41.62	40.34	35.34	32.84	33.06	33.68
	a	-8.52	-6.68	-3.95	3.62	6.93	6.51	17.16	18.48	21.10	16.18	11.80	1.64
	b	14.61	22.08	27.67	37.82	38.49	33.53	20.57	16.28	-1.09	-11.03	-12.30	-13.60
	t(m,sec)	18.42	19.02	19.43	19.59	20.13	20.34	20.55	21.32	21.55	22.24	22.57	23.25
	Colour	green	green	yellow /green	yellow	yellow	yellow	orange	orange/purpl	purple	purple	purple	violet
3.50	L	56.77	55.66	54.10	50.99	49.07	45.68	44.58	38.99	36.98	35.22	35.38	34.71
	a	-7.39	-2.38	-1.01	3.09	7.59	12.72	13.69	18.34	18.34	14.90	4.70	0.88
	b	16.45	29.86	29.75	33.93	34.13	29.49	27.68	10.51	-0.16	-7.60	-11.11	-10.74
	t(m,sec)	16.12	16.34	16.47	17.05	17.27	17.57	18.02	18.36	19.06	19.32	20.05	20.45
	Colour	green	green/yellow	yellow /green	yellow	yellow	orange	orange	purple/or	purple	purple	violet	violet
4.00	L	54.99	56.04	54.22	51.70	49.44	46.30	44.57	40.92	39.64	37.71	37.95	39.61
	a	-5.17	-3.64	-0.90	3.97	7.39	11.61	13.97	16.42	17.12	13.08	9.06	2.86
	b	21.01	26.40	30.04	34.09	33.82	27.97	23.99	12.90	7.15	-4.95	-5.52	-5.53
	t(m,sec)	14.41	14.57	15.14	15.40	15.57	16.19	16.31	16.56	17.57	18.32	18.49	19.10
	Colour	green/yellow	yellow /green	yellow	yellow	yellow	orange	orange/purpl	purple	purple	purple	violet	violet
4.40	L	52.66	53.13	52.13	50.93	48.41	50.06	46.87	43.44	40.91	38.10	39.46	40.99
	a	-3.41	-1.74	0.48	2.69	7.08	8.84	10.41	14.41	15.66	10.73	8.76	0.66
	b	21.24	25.48	28.79	30.74	30.56	31.29	27.03	18.08	11.22	0.65	0.21	-0.33
	t(m,sec)	13.37	13.52	14.09	14.23	14.45	15.05	15.21	15.45	16.04	16.29	17.02	17.19
	Colour	green/yellow	yellow /green	yellow	yellow	yellow	orange	orange	purple	purple	purple	violet	violet
4.80	L	51.59	52.67	52.68	51.38	50.04	49.84	48.56	45.51	44.20	41.17	41.24	42.52
	a	-2.57	-2.00	0.10	1.73	4.66	6.35	8.85	11.19	12.93	11.53	7.76	2.41
	b	19.89	23.50	26.72	28.62	28.86	28.52	27.15	22.37	15.99	7.84	3.71	3.17
	t(m,sec)	12.57	13.12	13.27	13.42	14.01	14.11	14.25	14.48	15.05	15.36	16.38	16.20
	Colour	green/yellow	yellow /green	yellow	yellow	yellow	yellow	orange	orange	orange/purple	purple	purple	violet

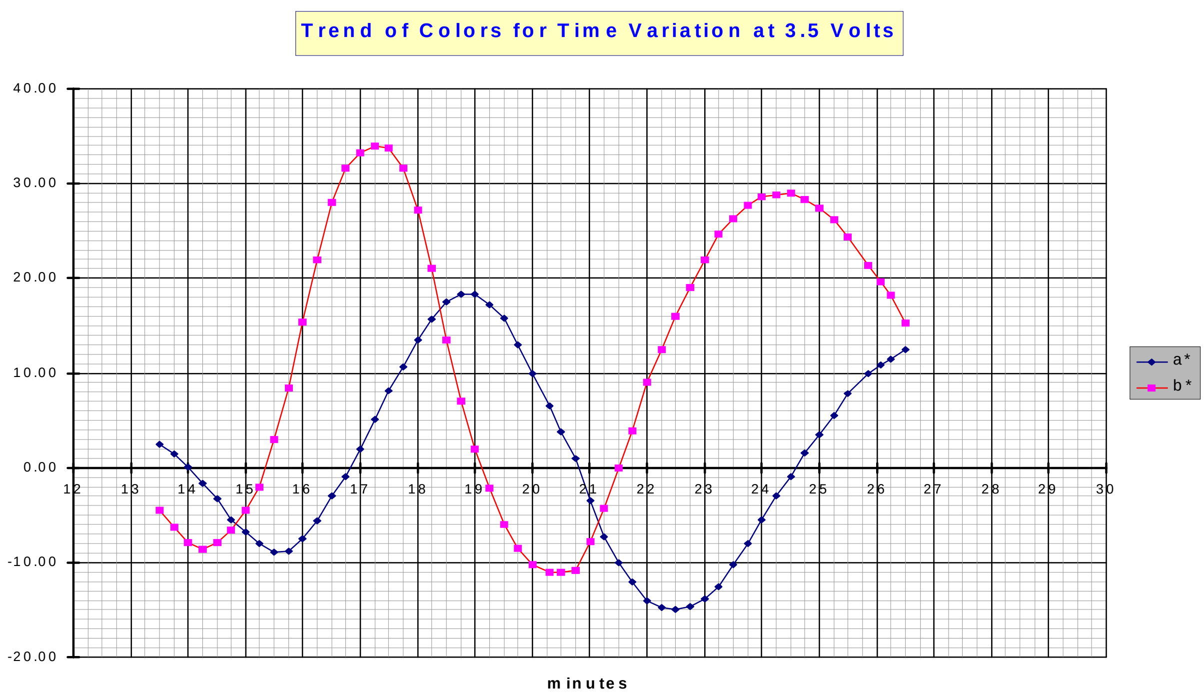
Table 4

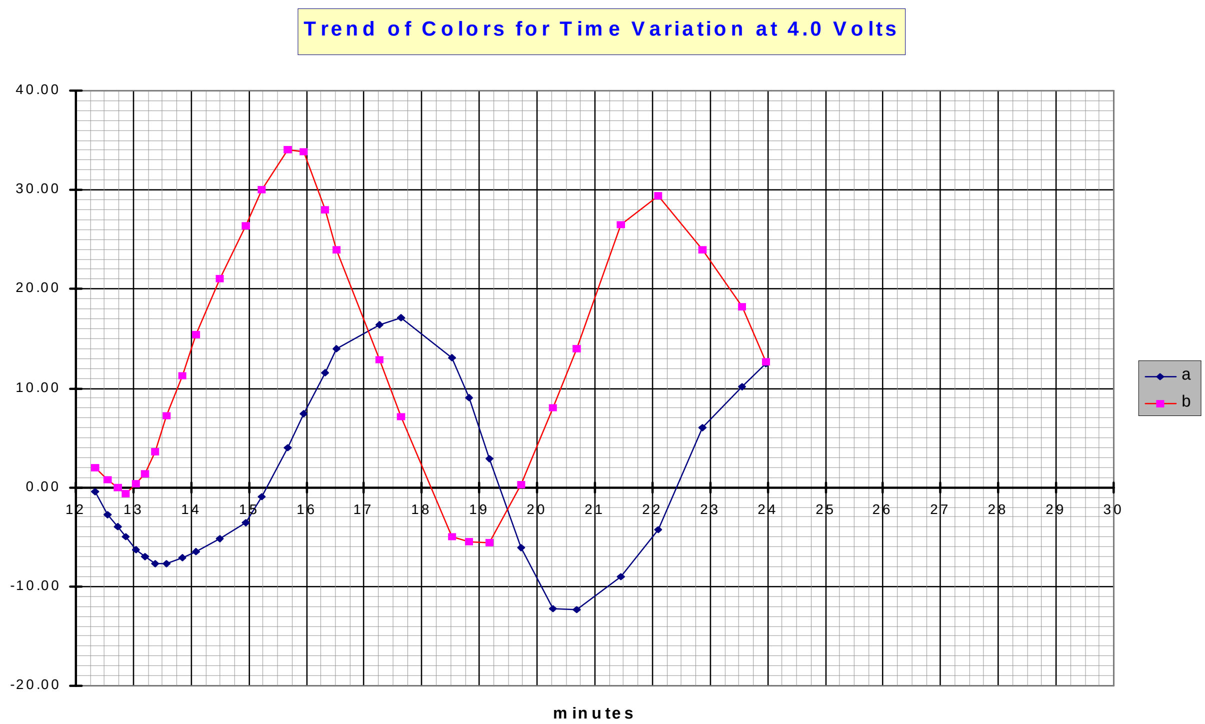
Volt	Code / Col. par.	5.25	5.50	5.75	6.00	6.30	6.60	7.00	7.50
3.00	L	37.40	40.61	42.42	42.56	46.27	47.70	43.82	42.44
	a	-6.15	-15.58	-18.45	-16.63	-11.59	-0.72	6.80	10.03
	b	-8.56	1.60	11.26	15.39	25.10	28.74	23.12	11.76
	t(m,sec)	24.03	24.46	25.22	26.05	26.35	27.32	28.27	29.49
	Colour	violet	green	green	green	green	yellow	orange	orange
3.50	L	38.75	44.51	45.80	47.06	47.25	47.01	46.28	43.28
	a	-7.74	-15.80	-15.18	-13.35	-5.37	0.18	9.94	11.27
	b	-4.72	8.81	15.05	24.30	29.16	28.89	21.36	15.21
	t(m,sec)	21.15	21.59	22.34	23.11	24.01	24.36	25.45	26.30
	Colour	violet	green	green	green	green/yellow	yellow	orange	orange
4.00	L	42.04	43.84	44.99	47.47	48.05	46.18	45.43	41.55
	a	-6.07	-12.24	-12.37	-8.96	-4.30	5.99	10.15	12.49
	b	0.30	8.08	14.03	26.52	29.45	23.92	18.18	12.70
	t(m,sec)	19.43	20.17	20.41	21.27	21.58	22.52	23.33	23.58
	Colour	green	green	green	green	green/yellow	yellow	orange	purple/oran.
4.40	L	42.24	44.09	46.00	47.49	47.24	46.84	47.54	45.65
	a	-4.24	-11.12	-10.70	-8.27	-4.76	2.46	6.77	10.17
	b	1.80	10.12	18.24	24.79	24.80	25.13	21.12	14.01
	t(m,sec)	17.52	18.23	18.57	19.26	19.54	20.38	21.27	22.21
	Colour	green	green	green	green	green/yellow	yellow	orange	purple
4.80	L	42.92	44.73	47.08	48.83	49.47	48.51	48.11	43.29
	a	-2.61	-7.82	-8.03	-6.09	-3.52	3.75	8.50	9.64
	b	5.75	12.69	20.35	24.83	26.75	23.77	19.90	15.07
	t(m,sec)	16.45	17.14	18.05	18.24	18.50	19.37	20.18	21.22
	Colour	violet	green	green	green	yellow/green	yellow/oran.	orange/purpl.	purple/orange

Graph 2



Graph 3




Trend of Colors for Time Variation at 4.0 Volts
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
minutes
a
b

Graph 4