New Developments in Aluminum Anodizing Methods—Hard Anodizing and Integral Color—Electrocoloring

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Some statistics of aluminum consumption will be given for conventional anodizing. Sulfuric acid, oxalic acid, chromic acid, integral and hard anodizing, modulated current anodizing for thyristor controlled rectifiers, electrocoloring topics of sealing hot and cold, electrophoretic and dip painting will all be discussed. Some novel applications, such as solid-type lubrication, pre-coated finishings and functional uses for electronics (in which Spain and the European Community are fairly advanced) will be introduced. Finally, applications of an alpha-alumina coating will be reviewed.

Some Statistics of the EEC Aluminium Import, Consumption and Recovery

EEC consumes about 2.5 million tons/year and formerly 1.7 million tons were produced domestically.However, due to high cost of electricity and of transportation of raw materials, recently nearly all alumina and reduction plants were scrapped or sold elsewhere in 1995, only 95.000 tons were produced which means the conservation of smelting technology only and 3.1 million tons of aluminium was imported and the rest were recovered scraps.

In 1995, 55.000 tons of Al cans were recovered among the totally used cans 115.000 tons (i.e, 47%) which means:

B/A = 666 KWH/23.500 KH 3 % (B: melting energy)

that is, the saving of 97 % energy could be obtained.

Table 1 shows the comparative data of various products anodized in various ways, as June 1986.

TABLE 1. Anodized Articles by Various Ways (unite: 1000 m^2/month)

	Sulphuric	Oxalic	Hard	Integral	Electro colour	Total
Daily commodity	357.8	33.8				391.6
Industrial	164.9	20.0	0.5			185.4
Architectural	3,185.7	28.6		28.6	4,942.3	8,156.6
Total	3,708.4	82.4	0.5	28.6	4,942.3	8,733.6

Anodizing Methods

Sulphuric Acid

Most common electrolyte is sulphuric acid with or without some additions, given transparent film which makes easier the further treatments such as dyeing, immersion colouring, electrocolouring, etc. The addition of a few % of oxalic acid is done to enhance film-forming efficiency in some factories. The addition of some alkaline sulphate particularly ammonium sulphate or ammonia gives the self-regulating capability of the electrolyte by keeping Al content at about 2-7 g/l level according to the temperature employed by gradual precipitation of low solubility ammonium alumina which is not only used for astringent or coagulator but also for raw material of artificial stones like scratch-free watch-glass (alpha -Al_2O_3), ruby, sapphire, topaz, alexander,etc. and for microtome for preparing electromicroscopic specimens. This kind of electrolyte can be used up to 35°C giving the film as same quality as normal sulphuric acid at 20°C or superior. The process is employed by order made curtainwall and window manufacturers, with subsequent electrocolouring and by some anodizers, without total replacement of the electrolyte which is usually done when Al content reaches 1-20 g/l in normal sulphuric acid electrolyte. A simple removal equipment is in the market.

Oxalic Acid

Oxalic acid anodizing had come into practical use by the invention of steam-sealing which plugs the pores by boehmite (AlOOH or $Al_2O_3H_2O$). This practise was started in Japan. However, due to the high cost of oxalic acid and high consumption of electric power (semi-barrier type), it gave way to sulphuric acid. Nevertheless, the process is still used for special purposes for its self-colouring yellowish shades, hardness, high-corrosion resistance, high electric resistant, high breakdown voltage, humidity sensor etc.

Chromic Acid

Chromic acid anodizing originated in England. The process has been used from time to time in order to get plastic-like shades together with dyeing for decorative purposes. However, we know that chromic acid film is rather ductile with negligible signs of crazing by not so strong mechanical deformation and the process has most recently found a new important applications in preparing aluminium hard memory disk by

anodizing high quality Al-Mg alloys in chromic acid (and sometimes plus sulphuric acid) to form 10 micron film followed by diamond cutting to surface roughness (Ra) below O.005 micron, above which 0.17 micron alpha-Fe_2O_3 is sputtered, which is converted to gamma-Fe_2O3 by heating up to 300°C. To prevent cracking, chromic acid fils was found to be best. Presently 200 megabit capacity is attained in 3.5 inch diameter disc.

Alkaline Anodizing

If anodizing is to be carried out in alkaline solutions, the anolyte close to the node would become nearly neutral, so that the pore formation would not be vigorous, which gives films of rather barrier nature. However, Sacchit and Ventura have succeeded in getting up to 10 micron films which can be electrocolour. Another merit is that the film is naturally alkaline resistant, while sulphuric acid film is easily soluble in alkaline environment, the fact being adopted for ESTAL-EEC specification for alkaline corrosion resistance test. One optimum condition is shown:

Electrolyte	NaOH 0.2 M, H_2O_2	2 %,
	$Na_4P_2O_7$,	0.05 %
Temperature	15°C, 45 V.	6 micron thick

A microscopic picture is shown in Fig. 1 as compared with chronic acid films for disks. Quite different structures from the normal ones are noted.

Subsequent electrocolouring conditions:

$NiSO_4$ $6H_2O$ 5%
H_3BO_3 10%
Triethanol amine 10%
pH = 8.L, 20°C, 25 V

Hard Anodizing and Integral Colour Anodizing

Hard anodizing is practically popular for engineering purposes. A thicker film means a hard film since by normal anodizing in sulphuric acid above 20°C or so, the formation and dissolution of the film are balance and usually 25 to 30 micron thickness is maximum, without cooling below 20°C. At higher temperature, for example, above 35°C, the oxide film finally disappears during electrolysis. As the film thickens, the colour changes from weak yellow through bronze to black. It appears there exists a colouring voltage when 4DC is used, while in the case of modulated current, even the anode voltage (cathodic polarization being negligible, the peak or surge voltage may happen to be 30 V). Thus coloured and hard films are available. However, in the case of sulphuric acid without any additions, the temperature must usually kept below 10°C. EEC has an ample experience of colouring in oxalic acid by the use of AC or AC + DC. Typical classifications of hard coatings are summarized in Table 2.

In the author's opinion, the so-called integral colour anodizing such as Kalcolor, Duranodic 300, etc., uses sulphonated aromatic acid or sulphonated higher aliphatic acid with a small amount of sulphuric acid. Aromatic or higher aliphatic group is of itself hydrophobic and together with their big size, they cannot enter into the anodize oxide. Only sulphonation makes them soluble in sulphuric acid solution. During electrolysis, the anodic films and the electrolyte are in a dynamic balanced state and the acid concentrations in the solution and in the films are nearly similar. Sulphuric acid film contains nearly 14 % sulphate and the integral colour films too. Organic groups only play a role of attaining the colouring voltage. The existence of excess Al in the film is playing a role of colouring When oxalic acid is gradually added to Dyranodic 300 electrolyte, the brownish colour disappears and yellowish oxalic acid colour appears. It is also clear by our experiments the cause of colouring is quite different between hard anodizing in sulphuric acid, integral colouring, and the oxalic acid films. The former two show no electroluminescence while the latter shows EL during anodizing and also shows photoluminescence (PL) by UV eradication on the film. As it may be clear now that chromic acid film contains ca. 3 % Cr_2O_3, oxalic acid film ca. 3 % oxalate and sulphuric acid ca. 14 % sulphate and hard sulphuric acid coating, integral colour coating contain Al and some sulphate. Therefore, integral colour coating electrolytes operation at 25-28°C, without strong cooling, may replace sulphuric acid hard coating below 10°C. The colour of oxalic acid film comes from another origin. Carboxulate oms which entered in the film is in an excited state (bluish EL, ca. 430 nm) and at about 40 V, they convert into tarry products resulting in yellowish or reddish brown colour. This film also belongs to 'semi-barrier' and may have 'colouring' voltage but the mechanism is totally different.

The author has classified 'Hard Coatings' as summarized in Table 2.

Improved Organic Acid Hard Coating with High Breakdown Voltage (High Dielectric Strength)

Column (B) of integral colour in Table 2 includes a newly developed organic acid process by Ventura and co-workers complying with the needs of hard, smooth, lustrous and high electric breakdown voltage from the EEC advanced electronic industry. A unique and creative designing in bath construction, cathode locations, racking and improvement of anode throw and way of cooling an clearing at least 5000 V/100 micron or more and Hv above 450oC. Incidentally, the electrolyte composition is similar to the proposed by P. Lelong and R. S. Segond and J. Herrenguel followed by E. Lichtenberger and Holo but the operation conditions and film properties are quite different:

Electrolyte Oxalic acid 80 g/l
Formic acid 80 g/l

Counter cathode: Graphite

Temperature 5-40°C C.D. 2-6a/dm^2, DC

Pre-Treatment

As pre-treatment, the elimination of acidic and alkaline fumes like NO_x, SO_x, etc., disposal of P and N compounds, waste recovery and recycles or non-utilization of such toxic material, halo gas is especially preferred. By degreasing with NaOH (with or without chelating agent like gluconic acid), the addition of sodium silicate precipitates sodium aluminium ortho-silicate (Zeolyte) and most of Na h and gluconic acid, if any, are recycled. Zeolyte is used in various ways such as adsorbent, builders for detergent instead of sodium tri-polyphosphate, the use of which in now prohibited in the EEC in order to prevent the growth of alga, weeds, etc, in rivers, lakes and inland sea. In order also to replace conventional chemical polishing baths, main constituents of which being phosphoric, nitric and sometimes hydrofluoric acids, the author proposed sulphuric acid based bath. Both acids are very similar in properties (chemical attack, viscosity and polish-capability). Only sulphuric acid on aluminium in severe. If this difficulty is overcome, the finish is rather clear than by phosphoric acid by which the finish happens to show iridescent (blue-reddish) tone which often strengthened by wiping. Sulphuric acid is added with magnesium, cobalt sulphate and some clathrate compounds like zeolyte referred to above will suppress the attack and absorbs acid gas and fumes. Of course phosphoric-nitric acid is easier to handle. Sulphuric acid gives very clear and brilliant surface. Zeolyte is also usable for suppressing alkaline fume by degreasing operation.

Table 3. Comparison of Sealing Effect

10 micron film, 10 min. sealing, ageing 1 day (36°C), no final sealing

	Corrosion Resistance	Degree of Sealing mg/dm^2	Additional Sealing hot water 60°C, 10 minutes
L-100 NiF_2, 5 g/l	50 s#	10.6	60 s
Zr-001 2 g/l	60 s	8.4	120 s

Corundum and Ruby Films

Anodized Al in the low temperature melts of bisulphate such as $NaHSO_4$, $KHSO_4$ and NH_4HSO_4. The simple salt or their mixtures melt at 100-1600. Cand anodizing was done with Ti as cathode in these melts at, say 1 A/dm^2 to form white extra-hard corundum films which can be made as thick as 100 micron or more. Sparking and luminescence are evidenced during anodizing. Theoxide consists of Alpha-Al_2O_3 which has been converted from the initial amorphous through gamma (face-centred cubic) to alpha-Al_2O_3 (close-packed hexagonal). This is a typical example of electro-oxidation and electro-thermic transition reaction at localized area of Al anode surface. Although the film is coarse and porous and ceramic-white) d=2.96 against compact corundum

(d=4.0) , it is dramatically resistant to tangential abrasion and chemically very stable, attacked neither by alkali nor acid nor even by HF. The film can be impregnated with oils, inorganic and other functional material. The corundum coating is finding applications in heat-resistant ductile Al wire for magnetic coils (500°C), business machine parts where extreme wear resistance is required, solid type capacitors. Cock et al. demonstrated a possible pretreatment to improve stress-cracking performance of Al alloys in aero-space applications.

The first conventional sulphuric acid to form porous type films which are then immersed in ammonium sulphate solution, subjected to anodizing in bisulphate melt. The films were converted to alpha type and doped Cr played a role of forming ruby film. The films are rather coarse and pinky, but under UV light irradiation, the film shows a fascinating deep red colour. They applied various salt solutions, but Cr gave best results. The process may be applied for decoration, illumination, electronics displays, laser applications, etc.

The Colouring of Anodized Aluminium

The process of anodizing aluminum goes back several decades,however several new advances and changing environmental needs have changed the colouring methods over the years. The purpose of this paper is to review the history and practices today as well as discuss what the future might bring.

Anodized aluminum can be coloured using the following methods.

.Chemical dyeing
.Adsorptive dyeing
.Electrolytic colouring
.Combination dyeing
.Interference colouring
.Other colouring methods

Integral Colouring

Integral colour anodizing took advantage of the metallurgical history of the aluminum alloy being coloured.It also made use of organic acids in conjunction with sulphuric acid. The process became unpopular during the energy crisis due to the fact that high current densities were employed to achieve the desired "earth tones".

From a finishing standpoint, the process was touchy and required constant monitoring. It was also very alloy dependent,which helped lead to it's demise as a popular finishing process. Electrolytic colouring (which replaced integral colouring) gave all the advantages without all of the headaches.

Chemical Dyeing

In this method of colouring the colouring matter is distributed in the hard aluminum oxide and is inseparably bound to the aluminum.

The most common colour using this method is various shades of gold that look like brass. The brass shades are produced using either ferric sodium oxalate or ferric ammonium oxalate. The ferric sodium oxalate chemical seems to be more stable in the tank and is also more desirable from the environmental aspect. Other colours like bronzes and greys can also be produced using this method buy are not very popular.

Electrolytic Colouring

This method of colouring utilizes alternating current in a metal salt solution. The anodic coating which acts as a capacitor rectifies the current at the barrier layer and alloys positively charged ions to electrodeposit at the base of the coating,this metal at the base causes the light to scatter and the degree of scattering determines the colour obtained. Generally, the lower the deposit content the lighter the shade.

Using electrolytic colouring can be done using several metals like Co, Ni, Cu, Ag, Sq, etc. However, the most popular method uses Sq as the metal of choice. Advantages and disadvantages of colouring using stannous sulphate are as follows:

Advantages

.Most conductive
.Easily available
.Less sensitive to contaminants
.Shades produced are widely used in practice
.Colours are very stable
.Sq is not a regulated metal in most treatment facilities.
.Multiple colours from one tank

Disadvantages

.Blacks are harder to obtain
.Sq is unstable and so chemical depletion is high
.Breakdown products sometimes difficult to filter
.Capitol investment in electrical equipment

required.
.Cannot use titanium racks.
.Load size is limited as compared to dyes.
.Limited colour shades available.
.Common stabilizers for Sq are phenolic and not desirable.

Adsorptive Dyeing

This method of colouring is the oldest and most widely used. The chromophore of the organic dye is adsorbed throughout the coating and is inseparable after the coating is sealed. The light fastness of the colour is dependent on the amount of dye adsorbed into the coating. Factors that effect dyeing are as follows:
.pH
.Water quality
.Temperature
.Dyeing time

The advantages and disadvantages of organic dyeing are listed below.

Advantages

.Very widely used and accepted.
.No need for additional capital equipment
.Reduced tooling costs
.Wide range of colours
.Excellent colour stability can be obtained with several dyes.
.Blacks are deeper and more intense.
.Excellent colour stability can be obtained with several dyes.
.Blacks are deeper and more intense
.Excellent weathering characteristics can be achieved.
.Decades of experience on applicability.

Disadvantages

.Improper dyeing can cause fading
.Sealing mechanism more critical
.Some dyes contain chrome complexes.
.Need for waste treatment.

Combination Colouring

This method combines the benefits of electrolytic colouring and organic dyeing to broaden the range of colours that can be obtained.

The electrolytically coloured deposit which is at the bottom of the coating is applied first followed by organic dyeing.

The advantages and disadvantages using this method are listed below:

Advantages

.Wider range of colours
.Colours are more muted
.Very light and weather fast colours can be obtained.
.Minimum capital investment required.
.Excellent field data on performance available.

Disadvantages

.Need for aluminum tooling
.Dyes are metal complex
.Sealing very critical.

Interference Colouring

This method was invented several years ago but has not found widespread applicability because of the complexity of the method. The method involves a reanodizing stage after the conventional anodizing to modify the pore structure. The modified pore structure causes an additional level of interference to the flow of light.

This can produce shades of blues, greens, greys and essentially any colours in the spectrum. The advantages and disadvantages are listed below.

Advantages

.Several colours can be produced from one tank
.Colours are light and weather fast
.Electrolytic colouring method well accepted.

Disadvantages

.Process involves several additional tanks
.Additional electrical needs
.Colour difficult to control
.Phosphoric acid in reanodizing step difficult to rinse
.Sealing method very important
.Poor throwing power of colouring tank.

Other Colouring Methods

Several other methods are published and patented which use different wave forms and combination of different chemicals that claim to produce colours in the blue and green shades. Some of these are not practical because of the complex

electrical requirements and because of the complexity of scaling up using alternating current. A process that we are working on produces shades of blues, greens and greys using techniques that do not require an additional reanodizing tank. With this method we can broaden the range to include blues, greys and greens. There is extensive work going on with different colours using electrolytic methods and the future looks very promising with this technology.

Table 4. Concentrations Electrolyzing Baths

Bath	Concentration	Bath	Concentration	Bath	Concentration
H_2SO_4	pH = 1.5	$ZnSO_4$	25 gr/l	$NiSO_4$	25 gr/l
				H_3BO_3	25 gr/l
H_3PO_4	15 ml/l	$Al_2(SO_4)_3$	15 gr/l	$NiSO_4$	25 gr/l
				H_2SO_4	Ph = 1.5
H_3BO_3	25 gr/l	$Al_2(SO_4)_3$	15 gr/l	$NiSO_4$	25 gr/l
		H_3PO_4	15 ml/l	H_3BO_3	25 gr/l
				$Al_2(SO_4)_3$	25 gr/l
$NiSO_4$	25 gr/l	$ZnSO_4$	25 gr/l	$NiSO_4$	25 gr/l
		H_3BO_3	25 gr/l	H_3PO_4	15 gr/l
				$Al_2(SO_4)_3$	25 gr/l

Other Functional Uses of Anodic Films

Since the oil crisis in 1973, the trends of the EEC aluminium finishing research has entered into a new era in addition to the traditional research and improvement of 'bulk finishing' for daily commodities, engineering, transportation and architectural finishing. It may be said ad 'functional *finishing of aluminium' particularly for electronics* and optics in which the EEC has some leadership in the world. They will be summarized briefly.

1. Dialectic characteristics: Electrolytic capacitor, Al-Ti sintered capacitor, copying drum, super-mini-chip *type capacitor* 3.7 *mm.* solderable.

2. Insulator characteristics: Anodized cable, printed circuit substrate, hybrid IC substrate (light weight, heat emission, EMI shielding).

3. Electronic conductivity characteristics: Very thin films for tunnelling, negative resistance element.

4. Magnetic characteristics:
Magnetic memory disk substrate magnetized plates.

5. Optical characteristics:
Coloured-electrocolouring for solar heat absorptive panel.

Artificial stones: ruby film, pearl-opal, *marble-tone.*

Photosensitive films.

Electrochromic display.

Transparent films: Laser propagation, optic switching.

Luminescence EL, PL displayers for two *or three dimensional* use.

Reflection: mirror, screening film for ECD.

6. Separation characteristics by the use of pores: Gas, solvent, isotope separation, super-microgrid.

7. Humidity characteristics: Humidity sensor, heat-exchanger, hydrophillic films for air-conditioner.

8. Chemical characteristics: Catalysis, enzyme-filled bio-reactor.

9. Hard coating, lubrication-function (MoS_2, metallic soaps in the pores).

10. Others: Micro-size adjusting, anti-bacteria film, infra-red emission function.

TABLE 2. Classification of Hard Coatings

Electrolyte	So-called Hard Coating	Integral Colour (A)	Integral Colour (B)
Electrolyte Temperature	Sulphuric acid 1-30 % (Basic acid) -5 /-20°C	Sulphonated Aliphatic or aromatic acid +sulphuric acid	Oxalic acid or other mixtures
Temperature	-5 -20°C	20-30°C	5-40°C
C.D. A/dm^2	- 3	1-2	1-5
Thickness μm	below 150	up to 4o for architectural	up to 500
Type	semi-barrier	semi-barrier	semi-barrier
Composition	Al_2O_3 + sulphate + Al°	Al_2O_3 + sulphate + Al°	Al_2O_3 + poly-metallized tarry products
Colour	Light brown, grey to black	Light, deep brown to black	Light yellow, gold, reddish brown
Origin of colour	excess Al° + some S in the film	excess Al° in the film	excited carboxyl (polymerized product)
Smell	deposited S, H_2S	--	--
Colouring-V	above 20 v	above 15 V	7 V especially AC
Luminescence	--	--	EL;Pl by UV
Roughness	becoming rough with thickness	rather smooth	smooth and lustrous
Cracks,Corners defect	many and brittle	many micro-cracks	apparently fe long streaks above 20 μm
Hv	300-350	350-400	above 450
Dielectric strength	not good 10-20 V/ μm, max.200 V so far attained	permissible	excellent 3000-4000 V (50 μm) >5000 V (100 μm thick)

For comparison: PVC 1000-1200/100 μm
Polyethylene 1200-1400/100 μm
Vinyl carbazole 3000-4000/100 μm

Table 2: Values of dielectric strength, apart from original properties, are dependent upon how thick, compact smooth (spacing), electrode pressure, humidity and DC or AC applied.DC or AC applied.

Summary

The grounding effect in anodizing or colour bath have a severe effect on colour formation that are consistent and reproducible. When grounding takes place in the anodizing bath, irregular oxide coatings are formed. When the aluminium is coloured, ¡uneven colour is obtained. It is observed that a 5 μm difference in the oxide coating thickness can produce a visible difference in the colour obtained.

Grounding in the colour bath results in longer colouring times and an apparent loos of throwing power.

It is very important for the anodizer to check tank connections and pin hole leaks in tank linings on a regular basis. All foreign objects that have been dropped into the tanks should be removed immediately. Good housekeeping procedures will pay off in eliminating potential problems and costly down time.

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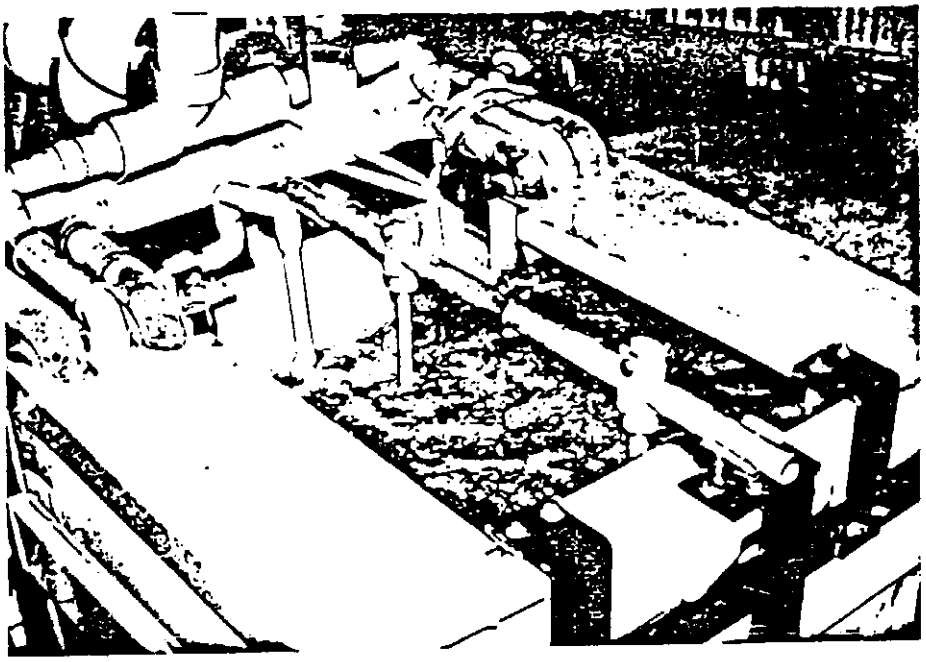


Fig.1

Fig.2

Fig.1 and 2 New Hard Anodizing Operation(12, 15)

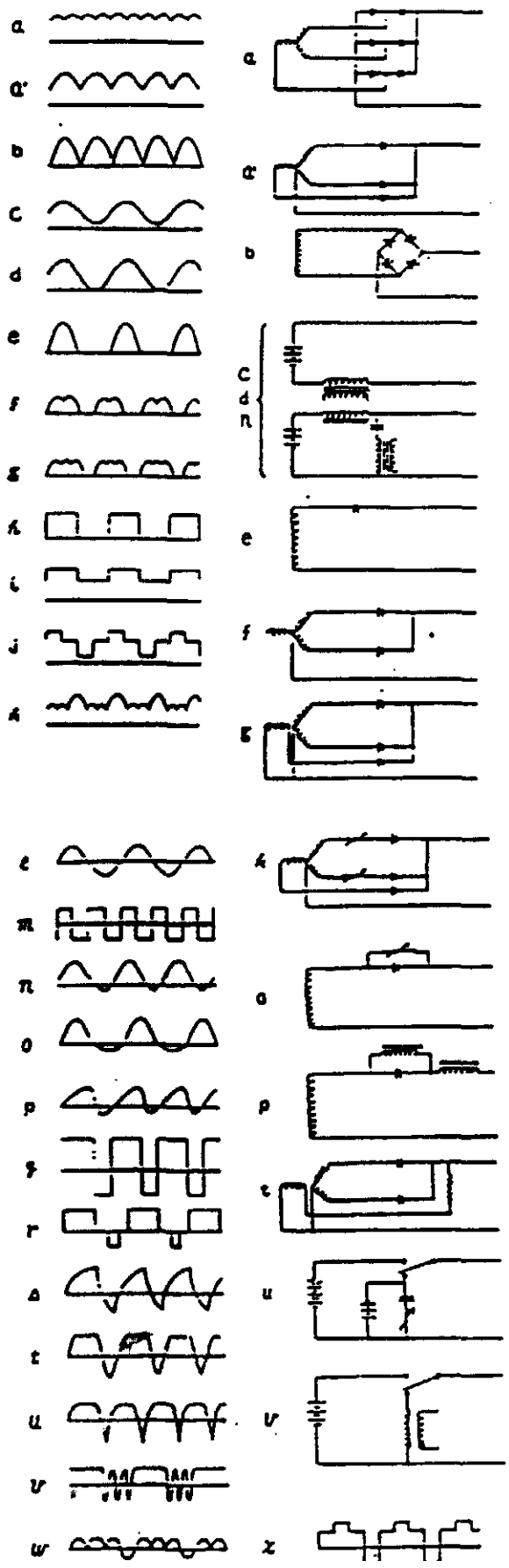
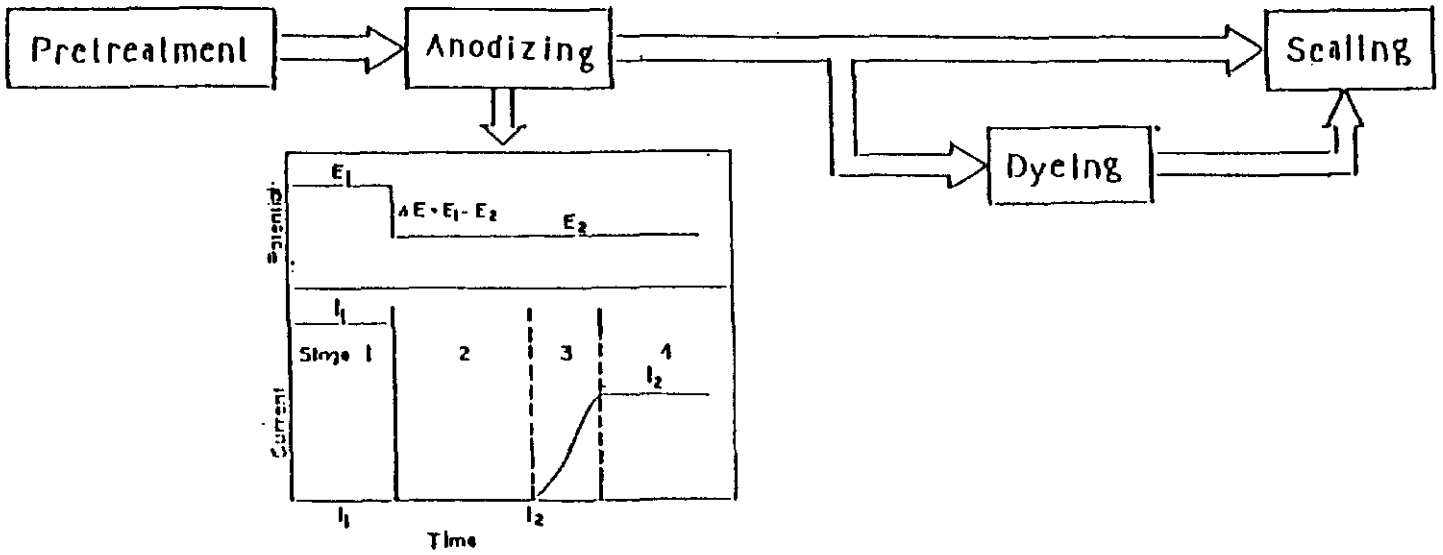
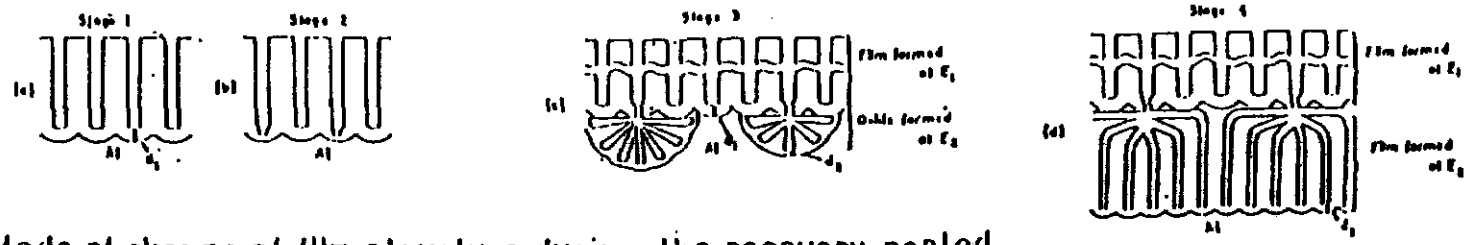


Fig.3 Imperfectly rectified (I.R.) Circuits

Fig.4 Integral color process by recovery effect



Characteristic change of current during recovery period.



Mode of change of film structure during the recovery period.
(pore branching)

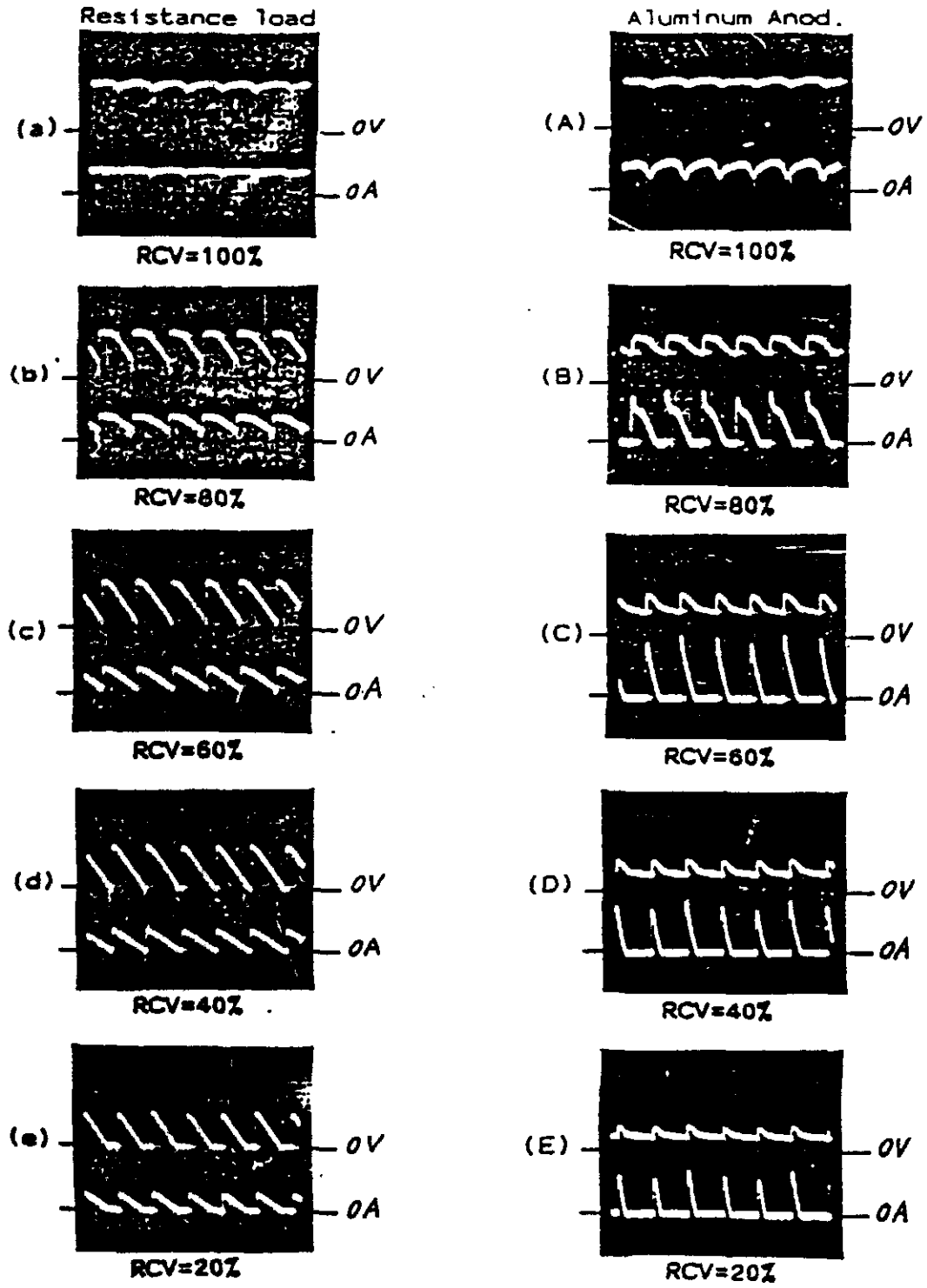


Fig.5 Specific Distortion of Wave Form by SCR

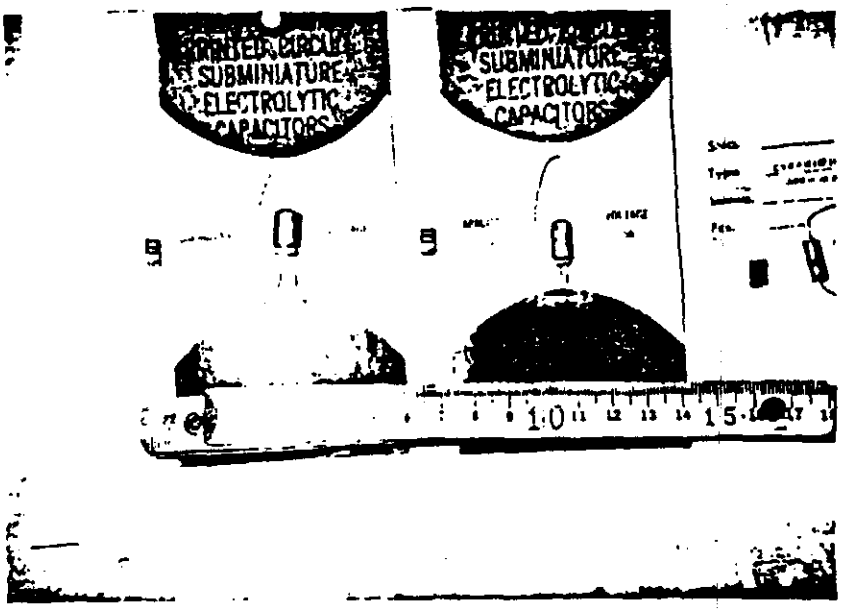


Fig.6. Subminiture Electrolytic Capacitors(1972).