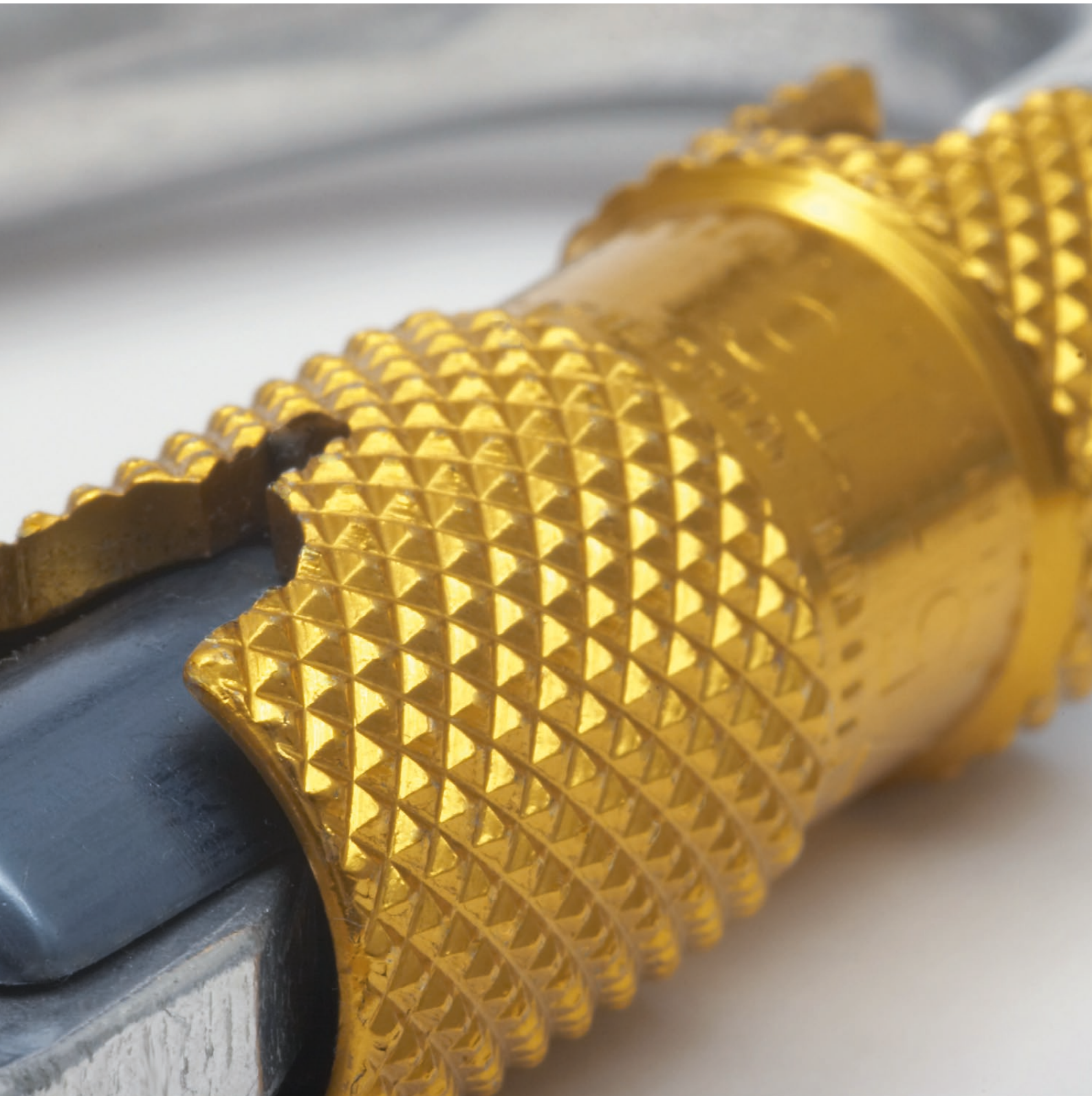


# VARIATIONS IN COLOR THE DYEING OF ANODIZED ALUMINUM



# THE DYEING OF ANODIZED ALUMINUM CONTENTS

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# VARIATIONS IN COLOR FOREWORD

**Color is an essential element of our lives.**

**For many years a number of coloring processes have been available for the color finishing of anodized aluminum.**



The following coloring processes have mainly been used in industrial practice:

- Inorganic
- Integral
- Electrolytic
- Interference
- Adsorption with organic dyes
- Overdyeing: electrolytic followed by adsorptive dyeing using organic dyes – Sandalor\*<sup>1)</sup>

However, for cost and ecological reasons, some of these coloring processes are hardly any longer used. Dyeing with organic dyes has become firmly established, thanks to a large number of high-quality products which allow any desired shade to be produced.

The following features are characteristic of anodic coatings dyed with organic dyes:

- The dyes are deposited into the pores of the organic anodic coating. The pores are subsequently closed in a sealing process
- The dyed coating is inseparably bonded with the aluminum. This is an essential difference from other coloring methods such as lacquering
- The dyed coatings exhibit high resistance
- The decorative appearance and the metallic character remain intact

The purpose of this brochure is to show the anodizer ways and means of further improving the reliability of adsorptive dyeing with the Sanodal, Sanodure and Sandoye dyes from Heubach and how to correct potential failures.

\*<sup>1)</sup> Trademark of Interogyd AG, Altenrhein, Switzerland



# PRINCIPLE OF THE FINISHING PROCESS

The dyeing process is intermediate between anodizing and sealing, the complete finishing sequence being as follows:

## A. Mechanical and chemical surface treatments

The final appearance of the metal is determined by grinding, polishing or brushing followed by cleaning, degreasing and etching to prepare the surface for the subsequent treatments.

## B. Anodizing

The electro-chemical formation, of a thick aluminum oxide film, the anodic coating. This is a prerequisite for adsorptive dyeing.

## C. Dyeing

The deposition of dye molecules in the pore system of the anodic coating.

## D. Sealing

Pore closure with irreversible fixation of the dye in the coating.

In this finishing system the main process steps and the intermediate treatments are the same as in straight anodizing without coloring, so the same guidelines have to be followed to produce a finish meeting the service specifications.

However, since adsorptive dyeing shows up deviations from the quality standard much more conspicuously than other coloring processes, it is generally found that narrower tolerance limits are necessary.

It is particularly important that the anodic coating should be of uniform porosity and thickness.

## ADSORPTIVE DYEING

In order to understand the mechanism of dyeing with organic dyes, we must recall the well-known picture of the aluminum oxide coating.

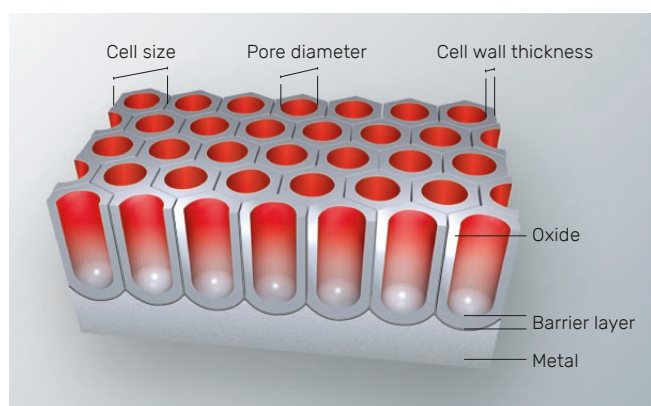
As is generally known, the anodic coating consists of an enormous number of hexagonal cells which stand vertical to the metal surface. Each cell contains a pore in its center. There are about  $10^{10}$  pores per  $\text{cm}^2$  of surface, with a diameter of 10 nm and a length of several 10000 nm (see illustration).

As we know, the pores of the anodic coating:

- Have a high adsorption capacity
- Improve the hardness and abrasion properties
- Allow dyeing with organic dyes

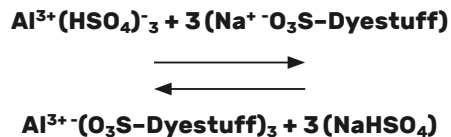
Let's now look at adsorptive dyeing with organic dyes the Sanodal, Sanodure and Sanodye dyes.

In the dyeing process the dyestuff molecules migrate into the pores of the anodic coating.



# PRINCIPLE OF THE FINISHING PROCESS

The adsorption of anionic dyes is mainly based on the exchange of the bi-sulphate ions with the dyestuff anions.



The bonding of the ions can be supplemented by additional bonding forces such as van der Waals' forces and hydrogen bridges. However, these forces are much less pronounced than with textile dyes, which is probably due to the fact that the aluminum surface is very rigid in comparison to cellulose or protein molecules.

As already described in the literature, a dyestuff molecule can be covalent-bonded or ionic-bonded, i.e. through an ion exchange with dyestuff anions or through an ion exchange with anionic dyestuff micelles (see illustration).

The linkage is not stable; rather an equilibrium is reached between the dye adsorbed on the surface of the anodic coating (intensity of the dyeing) and the concentration of dye in the dyeing solution.

If the dye concentration of the solution is increased, the quantitative adsorption also increases until the saturation point is attained (maximum color intensity).

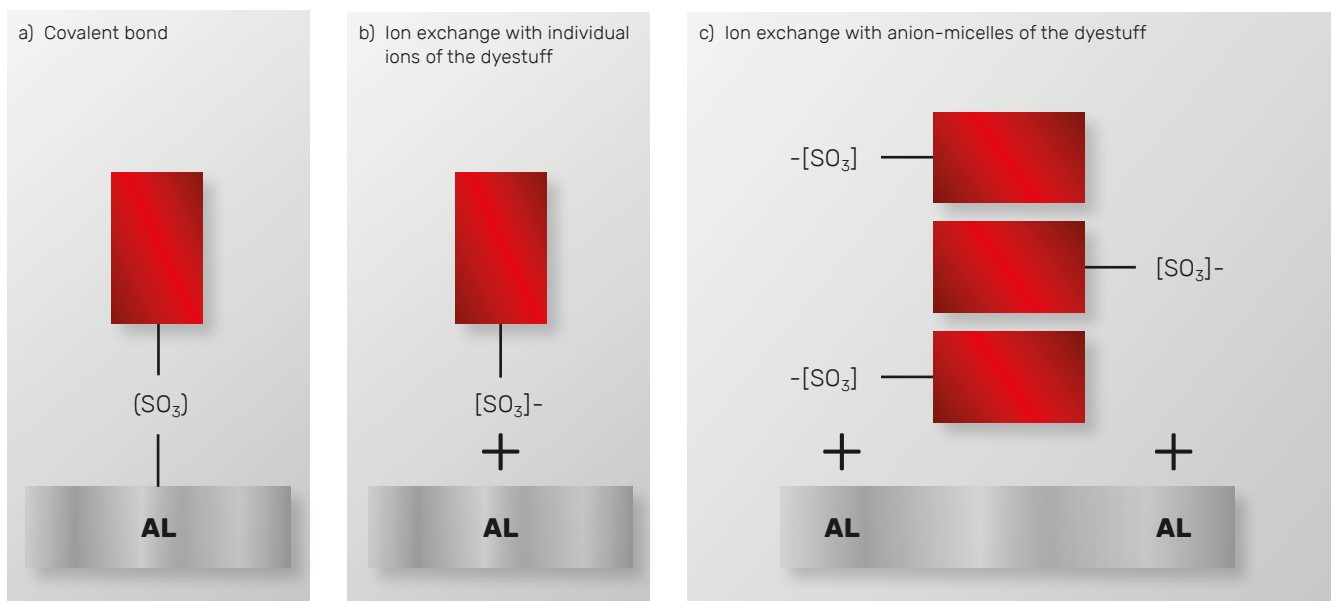
If the amount of dye in solution falls to, say zero (pure water), desorption takes place (bleeding, decolorization). It is therefore essential to seal the porous coating after dyeing.

The actual dyeing process can be broken down into three phases:

1. Migration of the dyestuff molecules into the pores.
2. Adsorption at the outer surface of the anodic coating
3. Diffusion from the outer surface through the mouth of the pore, along the pore walls into the interior of the coating. The rate of adsorption of the dyestuff is determined above all by the rate of diffusion of the dyestuff molecule through the pores. This migration takes place rather slowly.

When we recall the relation between the pore length of approx. 10000 nm and the pore diameter of 10-30 nm it is evident that the molecule size and functional groups constitute very important factors in the rate of diffusion and the distribution of the dye in the anodic coating.

## PROBABLE MECHANISM OF DYEING THE ANODIC COATING WITH SULPHONATED DYES



# SANODAL<sup>®</sup>, SANODURE<sup>®</sup> AND SANODYE<sup>®</sup> DYES

These three ranges differ from one another especially in respect of light fastness.



## APPLICATIONS \*2)

Sanodure dyes are recommended for aluminum products for everyday use such as household articles, jewelry, cosmetics, decorative articles, machine components, optical instruments, automotive parts, sports articles, multicolor nameplates, interior furnishings, etc.

For exterior architectural use, where high specifications with respect to light, weather and corrosion resistance must be met, the Sanodal dyes are exclusively suitable. Here special instructions must be observed with respect to processing and bath control.

The Sanodye range for use in sensitive applications contains dyes with heavy metal free structures only. Three of these dyes Sanodye Yellow 3GL, Sanodye Blue G and Sanodye Blue 2LW meet the high light- and weather fastness properties as required for outdoor use comparable to the Sanodal dyes.

## DYE SUFFIXES

The suffixes borne by our Sanodal, Sanodure or Sanodye brands generally have the following significance:

B	Bluish shade
C	Rapid rate of adsorption (suitable for continuous dyeing)
G	Yellowish shade
H	Notably heat resistant
L	Notably high light fastness
M	Mixture of dyes
N	Neutral shade
P	Phthalocyanine dye
R	Reddish shade
W	Notably high weather fastness

A figure preceding a letter suffix enhances its significance.

\*2) See also section 9.8

# 1

## ALUMINUM GRADES AND THEIR OXIDATION

The composition and grade of the aluminum alloy received for finishing are significant factors which have to be given due weight for success in adsorptive dyeing.

Pure aluminum contains no more than traces of other metals but is hardly used in industrial process due to mechanical weakness.

Since the intrinsic strength of aluminum is not sufficient for many uses, a high proportion is alloyed with other metals, which in the main are magnesium, silicon, manganese, copper or zinc. The higher the relative proportion of these constituents in the alloy, the greater is its resistance to mechanical wear, but its suitability for decorative color finishing is lessened to the same degree. Adsorptive dyeing does not in itself modify the physical properties of the anodic oxide coating.

### **Quality specifications**

To ensure the decorative appearance of the anodized and dyed aluminum surface, "Anodizing Quality" must be used.

### **1.1 EFFECT OF ALLOY COMPOSITION ON COLOR AND TRANSPARENCY**

The inherent color of aluminum and aluminum alloys varies with the level of purity and the composition respectively.

The shade of adsorptive dyeings is affected by this undertone.

- Magnesium in amounts greater than 5% dulls the anodic coating.
- Manganese and Chromium in amounts as low as 0.1% give the coating a yellowish cast, while greater amounts darken the tone of the metal.
- Silicon tends to impart a grayish cast to the coating, though a great deal depends on the form in which it is present in the alloy. If it is in solid solution in amounts to 1% it does not dull the coating appreciably. In amounts greater than this and in nonsolid solution it gives the metal a cloudy grayish color. One particular type made with 3–6% silicon is in fact known as a "gray tone alloy".



- Copper in amounts to about 0.2% has no visible effect on the color, transparency or hardness of the anodic coating. In the amounts in which it is commonly incorporated in alloys (the AlCuMg group and others) it gives the metal an irregular speckled, brownish and grayish appearance. Moreover aluminum-copper alloys are more prone than others to galvanic corrosion (pitting) in the dyeing process.
- Zinc has no effect on the quality of the coating. If the percentage content is around 2% or more and provided the alloy contains no other constituents, no significant shade differences or dulling of the dyeing are in evidence.

## 1.2 MECHANICAL AND CHEMICAL SURFACE TREATMENTS

Aluminum cannot be anodized and dyed without pre-treatment. Careful surface treatment is in fact a prerequisite for impeccable, level dyeings. The mechanical and chemical preparatory treatments grinding, brushing, polishing, etching determine the final appearance of the metal surface since its optical properties are not modified by the transparent oxide coating or by dyeing. The objective of the chemical treatments is to clear the metal from fats, oils, occluded impurities, grinding residues and the natural oxide film. If not completely removed, these contaminants obstruct formation of the oxide coating which later leads to visible imperfections in the dyeing.

For the preparatory treatment of aluminum parts intended for anodizing and adsorptive dyeing, the same guidelines apply as for anodizing without coloration.



# 1

## ALUMINUM GRADES AND THEIR OXIDATION

### 1.3 OXIDATION

A porous oxide film with a capacity for adsorbing the necessary amount of dye is required for successful dyeing. Since the natural oxide film formed from atmospheric oxygen does not meet this requirement it has to be replaced by a thicker artificially formed film. The methods employed for this purpose give oxide coatings which differ in their adsorptive capacity for dyes. Almost invariably, aluminum with a coating formed by anodic oxidation is used for color finished products with visual appeal.

### HEUBACH STANDARD COATINGS

All the information on anodizing given in our technical literature, unless otherwise stated, relates to the standard anodic coatings defined below. The thickness agrees with the average values for the coatings formed by the direct current (D. C.) sulphuric acid method, the one most widely used in the industry.

In the event of deviations from these standard anodizing conditions (see table below), the following sections should be consulted.

	STANDARD COATING	SANODAL STANDARD COATING
Sulphuric acid (free)	165–200 g/l	180–220 g/l
Aluminum content	5–15 g/l	5–15 g/l
Current density	1.2–1.8 A/dm <sup>2</sup>	1.2–1.8 A/dm <sup>2</sup>
Voltage	12–20 V	12–20 V
Current	D. C.	D. C.
Temperature	17–21°C/63–70°F	18–20°C/64–68°F
Time	25–35 min.	55–70 min.
Coating thickness	12 µm	25 µm

## **EFFECT OF THE ELECTROLYTE AND CURRENT ON THE DYEING PROPERTIES**

### **D. C. sulphuric acid process**

The direct current, sulphuric acid (Alumilite) process is preferable because it produces a coating with optimum properties for dyeing with organic dyes, namely high adsorptive capacity and transparency without any inherent color.

### **Modified D. C. process**

The modified D. C. sulphuric acid process allows for anodizing at higher current density (rapid anodizing) or higher temperature, without detriment to the decorative or protective properties of the coating. The modification consists in the addition of oxalic, citric or other suitable acid, which restricts pore formation and hence limits the adsorptive capacity of the coating for dyes. Given otherwise constant conditions, the dyeings are of lower intensity and are often less fast to light. For aluminum building elements that are to be color finished by the Sanodal system, an acid addition is not suitable as it leads to inferior light fastness.

### **D. C. oxalic acid process**

The D. C. oxalic acid process gives thicker coatings which have greater resistance to mechanical wear but much lower adsorptive capacity for dyes. The somewhat lower transparency and the likelihood of intrinsic color in the anodic coating are further factors that have to be taken into account.

### **Chromic acid process**

Anodic coatings formed with chromic acid (the Bengough-Stuart, Pigmental and Chromatal processes) are readily dye-able with Sanodure, Sanodye and Sanodal dyes. Applied on the opaque, milky gray coating, the dyes produce attractive enamel-like shades.

### **Hard anodizing process**

A hard anodizing process produces coatings which tend to show conspicuous self color and inadequate dye adsorptive capacity. They can however be dyed in a deep black with selected brands.

### **Integral color anodizing**

The colored coatings formed by the integral color anodizing process commonly used for architectural aluminum can be overdyed by the adsorptive process. This technique extends the range of colors for building fitments with a number of highly attractive shades. The black tone built up in the color anodizing process is sometimes found to be deficient in depth, in which case it is occasionally topped with an adsorptively dyed organic black.

### **Alternating current process**

The alternative current sulphuric acid (A. C.) process is used less often. The coatings formed are readily dyed with our dyes for aluminum; however, several dyes bleed heavily in the sealing bath.

## **EFFECT OF THE D. C. SULPHURIC ACID PROCESS PARAMETERS ON THE DYEING PROPERTIES**

It is very important to note that for the following: Adsorptive dyeing the final shade is determined by the dyeing process and to an equally great extent by the properties of the coating, including its anodizing parameters. When dyeing faults are being traced the anodizing conditions as well should be taken into consideration. Variations in the coating which are not brought to light by colorless anodizing tend to be accentuated by adsorptive dyeing and can be corrected only to a limited extent by modifications to the dyeing process.

# 1 ALUMINUM GRADES AND THEIR OXIDATION

## SYNOPTIC TABLE

PARAMETER	DEVIATION FROM HEUBACH STANDARD	DIFFERENCE IN INSENSITIVITY OF DYEING	DIFFERENCE IN MECHANICAL STRENGTH OF COATING
Sulphuric acid concentration	higher	deeper	lower
	lower	paler	higher
Aluminum concentration	higher	modified coating structure	
	lower	somewhat paler	somewhat higher
Current density (at constant coating thickness)	higher	paler	higher
	lower	deeper	lower
Temperature	higher	deeper	lower
	lower	paler	higher
Time	longer	deeper	higher
	shorter	paler	lower
Coating thickness	thicker	deeper	higher
	thinner	paler	lower

### Sulphuric acid concentration

An increase in the sulphuric acid concentration intensifies its dissolving action on the metal, producing pores of more markedly conical shape and of greater average diameter. As the increased porosity provides a greater inner surface area, the adsorptive capacity is enhanced allowing dyeings of greater intensity to be produced. During the service life of the anodizing solution more and more free sulphuric acid is expended in dissolving, and as the concentration declines so does the absorptivity of the coating. In order to ensure that successive dyeings are of equal intensity, it is most important to maintain the free sulphuric acid concentration within narrow limits.

### Aluminum content

The dye adsorptive capacity decreases sharply up to 5 g/l Al, but then remains nearly constant at higher concentrations. At over 15 g/l the solution does not work efficiently and there are likely to be irregularities in the anodic coating.

So in the interest of high color uniformity it is advisable to keep the content between 5 and 15 g/l aluminum.

### Current density

At higher current density and constant coating thickness the dye adsorptive capacity is lower since the metal is exposed for a shorter time to the dissolving action of the sulphuric acid.

In the joint anodizing of different alloys fluctuations in current density may occur between one part and another which are reflected in color differences when the parts are dyed. For this reason only one alloy should be anodized in a given batch; this is particularly important if the parts are to be dyed.

## **Voltage**

The voltage is given by the anodizing parameters and the composition of the alloy. It usually comes between 12 and 20 V.

## **Temperature**

A rise in temperature intensifies the dissolving action of the sulphuric acid resulting in softer, more porous coatings with higher capacity of dye adsorption. As the temperature has a very marked effect, close control is imperative. The tolerance limit is  $\pm 1^\circ\text{C}/1^\circ\text{F}$ .

In this connection it should be noted that if the heat convection is inadequate, local temperature variations may occur which later will result in unlevelled dyeings. To safeguard against the occurrence of local overheating there should be provision for thorough agitation and cooling of the anodizing solution.

## **Anodizing time and coating thickness**

The thickness of the anodic coating is almost exactly proportional to the product of the current density and the time. At constant current density (which is only approximately achieved in plant production), the coating thickness and consequently the adsorptive capacity for dyes are linearly proportional to the anodizing time.

It follows that fairly thick coatings are necessary if deep dyeings are to be produced. On the "Heubach standard coating" of  $12\ \mu\text{m}$  thickness virtually all desired shades can be obtained using suitable dyeing conditions.

However, with respect to light fastness which, as is well known, depends on the amount of dye deposited in the pore. In the case of high fastness requirements it is necessary to increase the coating thickness to  $22\text{--}28\ \mu\text{m}$ . For building fitments a coating thickness of  $25\ \mu\text{m}$  is compulsory <sup>\*3)</sup>.

Coatings thicker than  $30\ \mu\text{m}$  are not recommended for cost and quality reasons. On thin coatings of less than  $10\ \mu\text{m}$  the shade range is limited to pale tones because of the lower adsorptive capacity.

<sup>\*3)</sup> See section 1.3

<sup>\*4)</sup> See section 1.5

## **RINSING AFTER ANODIZING**

The rinse following anodizing is an important phase in the finishing sequence. If not removed, acid residues clinging to the dyed parts are liable to cause spotty dyeings.

They also contaminate the dye bath which leads to a gradual falling off in tinctorial power and may even bring about a chemical change in the dye. The aim should be to formulate an optimal rinsing treatment without excessive retention times, because otherwise there is a danger that the coating will be hydrated, i. e. prematurely sealed, which will reduce its power of dye absorption.

The efficiency of the rinse can best be controlled with the indicator bromocresol purple.

It is important that the fresh water should reach every point on the surface as speedily as possible. If the parts are of complicated shape with cavities, welds etc. This means that turbulence must be created in the rinsing tank.

To reduce contaminations, particularly sulfuric acid, cascade rinsing has proved to be a good choice. In cascade rinsing the anodized parts are dipped into tanks with less and lesser contaminated water.

Neutralization with an alkali such as diluted sodium bicarbonate is less to be recommended than rinsing.

Over-thorough rinsing may inactivate the anodic coating a little, but the effect can be offset by dipping the parts in an acid solution <sup>\*4)</sup>.



# 1

## ALUMINUM GRADES AND THEIR OXIDATION

### 1.4 STORAGE OF ANODIZED PARTS BEFORE DYEING

If anodized aluminum is stored for a time the adsorptive capacity for dyes diminishes, especially if the ambient temperature and the humidity are high. Anodized parts should therefore be treated further without undue delay.

If they are dried it is advisable to wet the parts with cold water or to activate them with acid <sup>\*5)</sup> before they are passed on for further treatment.

Anodized parts should not be allowed to become finger-marked. So far as possible they should be handled with damp rubber gloves. Areas that have been contaminated with dirt or grease do not accept sufficient dye for the required depth and cannot be sealed satisfactorily.

### 1.5 ACTIVATION OF THE ANODIC COATING

After anodizing and before dyeing, the coating can be activated by treatment in acid solution. Dilute nitric acid is generally preferred. This treatment invariably dissolves some of the material of the coating which increases its porosity and hence its dye adsorptive capacity. On parts that have been in store for some time, the dissolving action of the acid takes effect primarily on the hydration products formed by reaction with atmospheric moisture.

This increased adsorptive power for dyes can be of advantage for a number of reasons. However, at constant final thickness some deterioration in the quality of the coating must be accepted. Activation with acid is carried out mainly in the manufacture of nameplates.

#### Operating procedure

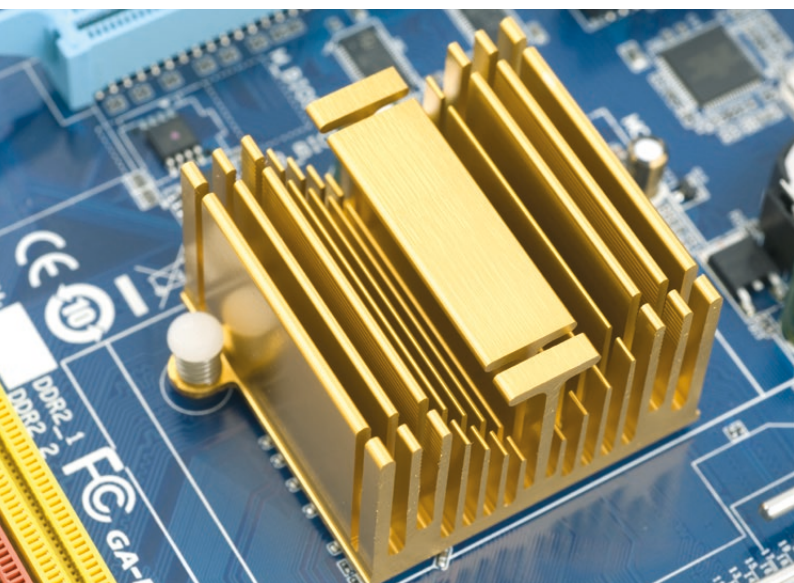
Immediately after anodizing or storing (moist or dried) the aluminum is treated as follows:

Solution	10–30 % nitric acid
Temperature	18–25 °C/64–77 °F
Time	10 s–2 min

These details represent examples of the treatment; the conditions may be adjusted to accord with other factors given by the finishing system. After activation the metal must again be thoroughly rinsed.

#### Properties of dyeings on activated coatings

Acid treatment under more severe conditions than the above can reduce the gloss and hardness of the coating as well as its corrosion resistance. For this reason acid treatment prior to dyeing is not recommended for architectural aluminum.



\*5) See section 1.5

# 2

## DYEING EQUIPMENT

The dimensions of the dyeing tanks and the volume of dye solution should be chosen so as to allow the batch to be fully immersed without having to re-arrange the anodized parts.

By employing the spray dyeing technique, dyeing can be effected with a very much smaller volume of dye solution (about 15–20 %, which is circulated with the aid of pumps and applied through spray nozzles).

### 2.1 DYEING TANK MATERIALS

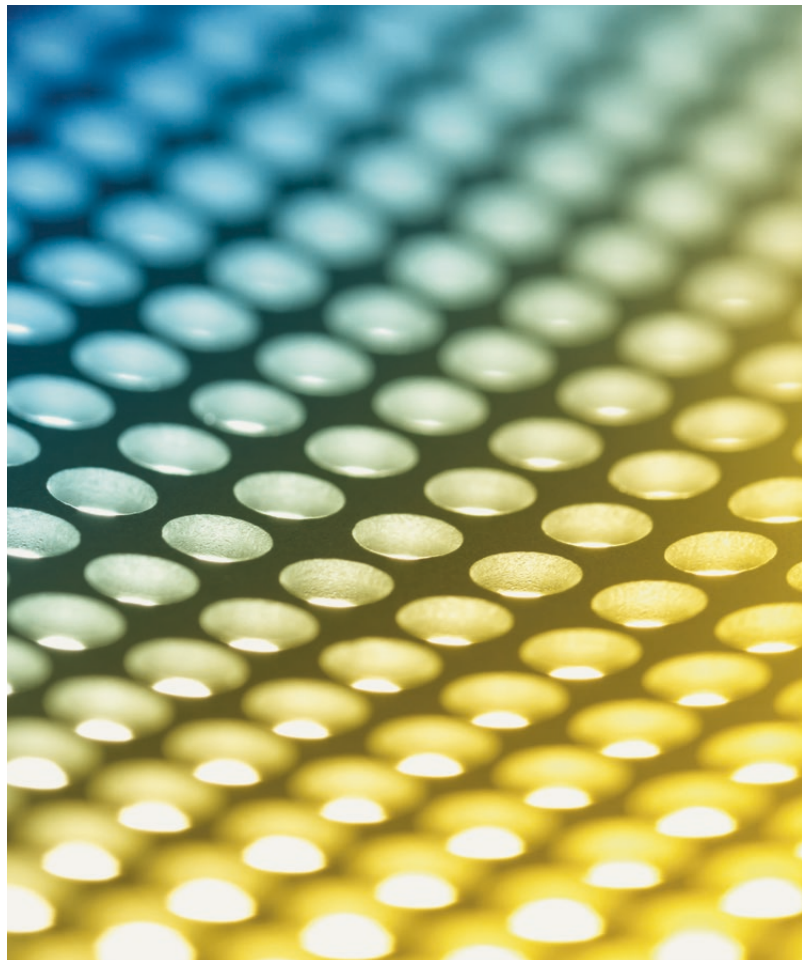
The tanks should be built with materials that meet the following requirements:

- Heat stability to 80 °C/176 °F
- Stability to diluted solutions of nonoxidizing organic acids
- Stability to chlorides at very low concentrations

#### **Suitable materials include:**

- Acid resistant stainless steel
- Plastics of medium to high heat stability such as polyolefins (polyethylene, polypropylene), polyvinyl chloride, polyacrylonitrile, polyester
- Hard rubber

Acid resistant stainless steels of the V4A type with a chromium/nickel/molybdenum base have given particularly good service.



# 2

## DYEING EQUIPMENT

### 2.2 BATH HEATING

The best system consists of electrical heating elements or heat exchangers fitted horizontally at a level close to the base of the tank. The heat conducting medium may be water, steam or oil. The heating system has to be built with materials that meet the same stability standards as those used for tank construction. It is necessary to equip the system with a temperature control unit as dyeing temperature is crucial for quality consistency.

### 2.3 BATH AGITATION

Moderate agitation balances the dye concentration throughout the bath and avoids concentration gradients.

The most popular method is generally the motion of the dye bath has to be increased by injecting filtered compressed air through perforated pipes. Another option are stirrers, e.g. propeller or rudder types, which give good service, especially with dyes that are sensitive to oxidation.

The dye bath can also be kept in agitation by a circulation pump. In this case a clearing filter can be inserted whereby the loose material in the bath can be trapped, thus ensuring a high degree of purity of the bath and the dyed parts.

First choice is the gentle agitation of the whole rack in the dyeing tank. The rate of adsorption falls off sharply as dyeing continues, so it is important to keep the bath well agitated, especially in the initial phase. With pale dyeings in particular, the levelness of shade can often be improved by moving the parts about in the bath immediately on immersion and during the first minute of dyeing.

### 2.4 ELECTRICAL INSULATION

If titanium jigs are employed jointly with metal dye tanks, particular attention must be given to avoid electrical contact.

Failing this, the dyed parts may be pitted through the formation of a galvanic current from the two metals and the dye solution. The titanium jigs should be insulated from the tank with a nonconductive material such as plastic before being suspended in the dye bath.



# 3

## EFFECT OF DYEING CONDITIONS ON THE COLOR

As in the case of the anodizing parameters, the dyeing parameters have a pronounced effect on the dyeings. The indications given here are to be regarded as general guidelines. For Sanodal dyeings the corresponding special directions must be observed.

### 3.1 DYEING TEMPERATURE

#### The rate of dyeing increases with increasing temperature.

The time required to produce a dyeing of a given depth is therefore shorter in inverse proportion to the temperature. The temperature dependence of the simultaneous sealing reaction, which slows down the rate of adsorption and under extreme conditions suppresses dyeing completely, is even more pronounced. If the temperature is too high, build up of the dye is halted before the full intensity is reached. The simultaneous sealing also impedes the reverse process of dye desorption.

Consequently dyeings produced at high temperature do not bleed so freely in sealing solutions or rinsing waters and are more difficult to strip. At room temperature the sealing action is weak, which means that deeper dyeings can be produced, but on the other hand the dyeing times are over-long. The temperature region of 50–60 °C/122–140 °F represents the optimum compromise between attainable depth and acceptable dyeing time.

50–60 °C/122–140 °F	Standard dyeing temperature.
Room temperature 20–25 °C/68–77 °F	For dyeings which are subject to be partially stripped (e. g. multicolor nameplates). For pale shades and dyes with insufficient heat stability.
	The lower rate of adsorption can be counter-balanced by higher dye concentrations or longer dyeing times.

# 3

## EFFECT OF DYEING CONDITIONS ON THE COLOR

### 3.2 DYEING TIME

**The normal dyeing time is in the range of 1-2 minutes per micrometer oxide coating thickness depending on the color strength desired.**

This is particularly noticeable when a mixture of dyes is involved. Color fastness considerations too make it not advisable to undercut dyeing times of 5 min, even for pale shades. Generally speaking, lower dye concentrations and longer dyeing times result in faster dyeings than higher dye concentrations and shorter dyeing times.

For color finished products which do not have to satisfy stringent color fastness specifications, the dyeing time may be reduced by a considerable margin, though this entails using more highly concentrated dye solutions. Very short dyeing times of a few seconds may cause many of the dyes to bleed heavily in the sealing solution.

The brands with the "C" suffix are adsorbed very rapidly so the dyeing times can be very short. The inorganic brands such as Sanodal Gold 4N can be applied in a short cycle of e.g. 30 s to 5 min duration, without endangering the light fastness of the dyeing.

### 3.3 pH VALUE

The optimum dyeing pH normally comes within the range of 5 to 6. A certain number of dyes require a value between pH 4 and 5 in order to build up satisfactorily in the pore system \*6).

As a rule the adsorptive capacity of the anodic coating increases with decreasing pH value, since the higher hydrogen ion concentration supplies a greater area of positively charged surface to which the negatively charged anionic dye is attracted and adsorbed.

There is however a lower limit to the permissible pH, since partial dissolving of the coating sets in below pH 4. Even at values above pH 4 minute amounts of aluminum may be dissolved which form precipitates or partially inactivate the dye. Moreover at such low pH values certain dyes are chemically unstable or precipitate owing to the consequent decrease in solubility.

### 3.4 DYE CONCENTRATION

The dye concentration has to be selected so that under the process conditions (pH, time, temperature) the specified intensity is obtained.

Best results are obtained when the aluminum is dyed at a low dye concentration and extended dyeing times.

In accordance with the laws of adsorption, under a given set of conditions the quantitative adsorption of dye on an anodic coating increases with increasing amount of available dye. However this rule applies only up to the point at which the adsorptive capacity of the coating is exhausted. Beyond this point an increase in concentration does not give a dyeing of greater intensity. On the contrary, loss of depth is occasionally observable owing to competition between the dye and colorless impurities for adsorption sites.

\*6) See also section 4.1



Dyeing solutions which are contaminated by impurities lose their dyeing power very rapidly and must be renewed.

Thus the cost of an adsorption dyed finish depends only partially on the dye consumption. Much more decisive are factors such as avoiding dragged-in foreign ions, which can be effectuated by efficient rinsing.

The price/effectiveness ratio of two dyes can therefore be compared only on condition that the exhaustion of the baths after a lengthy spell in use is included in the calculation.

The dye concentrations in g/l given in our shade cards and other technical literature normally apply for a dyeing time of 15 min at 55–60 °C/131–140 °F. As a rule they relate to "standard coatings" of 12 µm \*<sup>8)</sup> thickness.

On thicker coatings shades of equal intensity can be produced with lower dye concentrations. At constant dye concentration deeper shades are obtained on thicker coatings than on the standard coatings.

### 3.5 IMPURITIES

Impurities dissolved in the dye bath in the form of ions affect the dyeing process. These impurities often compete with the dye for adsorption sites which results in shades lacking the required intensity. Residues of monovalent acids such as nitrates, acetates and formates are not damaging and may even promote dyeing. Chlorides are dangerous as they cause galvanic corrosion. So are multi-valent anions, especially those that form complexes such as phosphates, silicates and fluorides; if present in only minimal amounts they are likely to block dyeing completely.

The impurities occurring most widely in practice in finishing solutions are sulphates and aluminum. The dyes vary in sensitivity to dissolved impurities \*<sup>9)</sup>. When the accumulated impurities exceed a certain limit, the bath must be renewed. So as to achieve the longest possible service life of the baths, the level of impurities must be kept to a minimum.

#### **To this end the following action should be taken:**

- Rinse the anodized parts thoroughly before dyeing to minimize drag-over of sulphates, aluminum and other ions into the dye bath
- Maintain the dye bath at the recommended pH to avert contamination by the dissolving action on the coating occurring at lower pH values
- Provide covers for the dyeing tanks when not in use to prevent contamination by treatment solutions dripping from raised parts
- Set the dye bath with selected chemicals to maintain it in good condition
- Carry out partial renewal of the dye bath at regular intervals.

Undissolved impurities do not affect adsorption but they tend to interfere with dye diffusion into the interior of the pores. Soil and more especially oil particles adhere to the anodic coating where their reserving action leads to un-levelled cloudy dyeings or to poor film formation. Colloidal impurities penetrate into the pores and block dye diffusion. In spite of adequate dye concentration and dyeing time, this can prevent the dye from building up to the specified intensity. It is of the utmost importance to use oil-free compressed air for bath agitation so as to keep the bath free from oil particles.

\*<sup>8)</sup> See also section 1.3

\*<sup>9)</sup> See also table 9.3

# 4

## DYE BATH CONTROL

Uniform dyeings can be expected only if the coating properties are constant on the single part, from one part to another, and from batch to batch. The factors which determine the uniformity of anodic coatings have already been named and can be taken as known. Any variations in the formation of the coating are rendered much more conspicuous by adsorptive dyeing than by colorless anodizing or electrolytic metal salt coloring, so a higher standard of uniformity is necessary than for the latter processes.

### **The dye penetration is influenced by**

- Temperature
- Time
- Dyeing pH/buffer
- Dye concentration
- Dyeing power

Due to dye absorption, the introduction of impurities and partial bath renewals, the concentration is subject to constant change. The addition of further dye to restore the initial concentration is not enough for correction because the dyeing power steadily diminishes through the growing content of dissolved impurities. The percentage ratio of the dye adsorbed from a freshly prepared solution of the initial concentration and the dye adsorbed from a contaminated bath is termed the "relative dyeing power". The concentration of the two baths need not necessarily be equal.

To compensate for a decrease in dyeing power, sufficient dye has to be added to give a concentration in excess of the starting value, and/or the dye bath has to be partially renewed. If the conditions are extreme a fresh bath has to be set. The adjustment can be effected empirically or as indicated by the results of the tests described in the following <sup>\*10)</sup>.

### **4.1 DYE BATH pH**

#### **Measurement**

Electrical pH meters with glass electrodes are the most suitable type for determining the pH of aluminum dye solutions. The simpler method of measurement using color indicators is applicable only on a limited scale because of the self-color of the solution. The pH value may be measured in the dye bath but it is better to use a sample cooled to room temperature.

#### **Intrinsic pH of the dyes**

The intrinsic pH of a given brand depends on the concentration and the water hardness. The values are listed in section 9.2.

#### **Recommended pH ranges**

Section 9.2 gives an optimum pH range and buffer for each dye. For most brands this is pH 5 to 6.

#### **Adjustment and stabilization**

As the pH of the dye bath is unavoidably and repeatedly shifted by hard water, drag in of anodizing acid, evaporation etc., it is advisable to stabilize the pH value with a buffer. A buffering addition ensures that the pH will stay constant over a long period of time so that the dyeings agree in shade and depth from batch to batch. It also levels out color differences on a single part or between the parts in a batch arising from local pH fluctuations. These differences are most often due to inadequate agitation or to the parts being of complicated shape with cavities or the like.

Most of the Heubach aluminum dyes must be buffered with sodium acetate buffer (pH 5–6). For some dyes ammonium acetate buffer is advantageous and several grades are not buffered at all. pH and buffer addition for all dyes can be found in table 9.2.

For pH correction ammonia or dilute caustic soda is used to increase pH, while acetic acid is used to reduce pH. Only in the case of Sanodal Gold 4N sulfuric acid is necessary for reduction of pH instead of acetic acid.

<sup>\*10)</sup> See section 5.3

## 4.2 DETERMINATION OF DYE CONCENTRATION

Detailed instructions for determining the dye concentration in the dye bath can be found in our product sheets.

### Visual determination of dye concentration

The intensity of a control solution and of a used solution which have been diluted by the same factor is assessed by visual examination. The more deeply colored solution (as a rule this is the control) is diluted with water until it corresponds in intensity with the other. From the volume of the two solutions the concentration difference is calculated.

### Spectrophotometric determination of dye concentration

The extinction value (extinction = decrease of light) of a dilute sample of the dye bath is measured comparatively with that of a control solution diluted in the same ratio and having the specified (nominal) initial concentration of the dye under test.

From a comparison of the extinction values, the actual dye concentration of the plant dye bath is calculated according to following formula:

$$C = [(E \cdot C_n) / E_n]$$

C = Dye concentration in g/l of dye bath

C<sub>n</sub> = Dye concentration in g/l of comparison

E = Extinction of dye bath

E<sub>n</sub> = Extinction of comparison

However, this very accurate and rapid test method only gives the total dye content; it does not indicate foreign substances which may still be present in the dye bath (e.g. aluminum sulfate, etc.), and which can impair dye adsorption if present. For this reason it is necessary to determine the actual dyeing power of the bath.



# 4

## DYE BATH CONTROL

### 4.3 DETERMINATION OF DYEING POWER (ACTIVITY)

This important dyeing factor can be determined either by visual scrutiny or by spectrophotometry. The visual test gives only approximate values.

#### Visual determination of dyeing power

In the laboratory a dyeing from a freshly prepared solution of the initial concentration and one from a sample of the used dye bath are produced under identical conditions. By visual comparison the intensity difference is estimated, from which the dyeing capacity of the used dye bath is assessed.

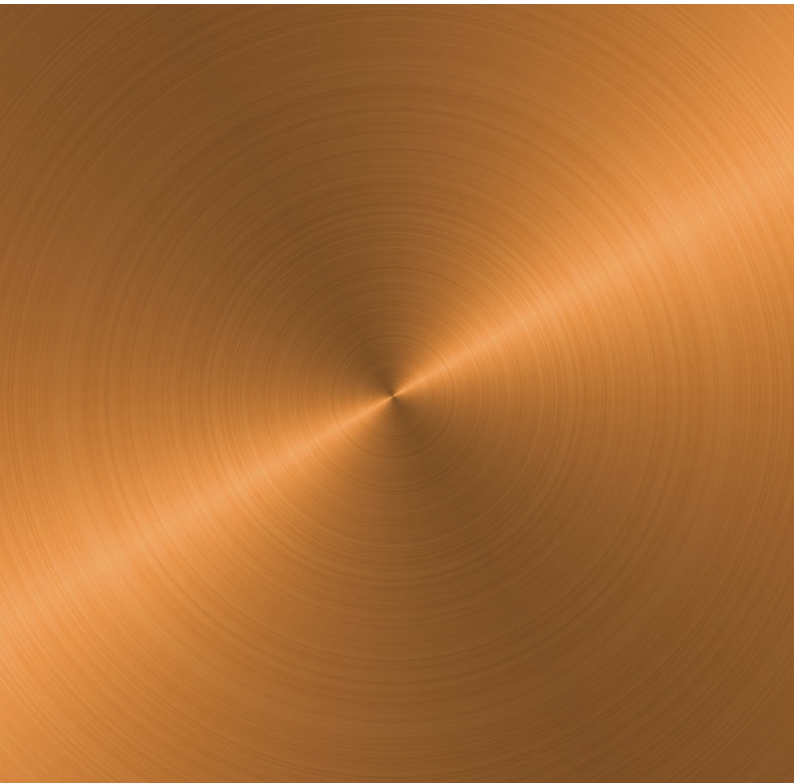
#### Spectrophotometric determination of relative dyeing power

The amount of dye adsorbed in the anodic coating from a freshly prepared standard solution is compared with the amount adsorbed from the bath in use in the plant. The dyeing conditions in the two baths may differ, e.g. the dye concentrations may be unequal.

The two dyeings are stripped, extraction solutions prepared under constant conditions and the extinction values measured. The quotient of the extinction values is a measure of the loss in dyeing power of the used bath. From this finding the relative dyeing power is calculated as a percentage value, from which is estimated the amount of dye which should be added to the bath.

Determination of the relative dyeing power is therefore of decisive importance because, unlike concentration determinations, it gives information on the actual state of the bath in service.

This test method is used mainly in cases where the finished product must meet high fastness requirements.



# 5

## PREPARATION, MAINTENANCE AND SERVICE LIFE OF DYE BATHS

### 5.1 WATER QUALITY

For dissolving the dyes and setting the dye baths, deionized water is highly recommended. With many dyes, hard water causes a reduction of the adsorption power. Water of poor quality leads to heavier bleeding in the sealing bath <sup>\*1)</sup> and therefore paler dyeings; it may also cause precipitation and bath turbidity.

Water containing softening agents is unsuitable. Special care should be taken to see that the water is largely free from chlorides, phosphates, silicates and iron. Water sterilized by chlorination is suitable.

### 5.2 SETTING THE DYE BATHS

When setting the dye baths, care must be taken that the dyestuff is well dissolved. It is preferable to dissolve the dyestuff with hot water (80–90 °C/176–194 °F) in a separate container (using about 5 parts water to 1 part dyestuff). With the dye bath agitation switched on, the clear stock solution is poured into the water through a fine screen, e.g. a gauze filter, in order to trap any undissolved particles. The bath is agitated for 15 min until fully homogenized. If a buffer is used it should be added before the dye. Finally the pH is checked and if necessary corrected, then the bath is brought to the dyeing temperature.

The Sanodure, Sanodye and Sanodal dyes are generally readily soluble in water. A few dyes, for example Sanodye Blue 2LW and notably Sanodye Blue G, are not fully soluble in the amounts of water recommended for stock solutions. These dyes are added to the water bath as they are and the suspension is first brought into an even state of distribution before heating to dissolve. The state of the final solution is tested with a sample.

Experience has shown that a freshly set bath does not develop its definitive dyeing properties until a certain time has elapsed, so it is advisable to prepare the bath a few hours before use. This is particularly recommended in the case of Sanodal Deep Black MLW. The waiting time can be shortened by heating the bath up to a temperature of 80 °C/176 °F. Liquid dyes can be added directly without pre-dissolving.

### 5.3 CORRECTION OF THE DYEING POWER BY PARTIAL RENEWAL OF THE BATH

Since dyeing solutions are exposed to changes in composition, it is imperative to control the dye concentration and the dyeing capacity, i.e. the state of the dye bath.

The concentration gradually declines as more and more dye is adsorbed by the coatings; the deficiency is made good by adding the amount of dye which is necessary according to the concentration test.

But at the same time the dyeing power of the dye solution decreases owing to the drag-in of inhibiting impurities, notably aluminum and sulphate from the anodizing electrolyte, which may reduce adsorption in spite of adjusting to the initial dye concentration. In this case it is essential to offset the reduced dyeing power at least partially. This is achieved by removing a portion of the spent dye bath at regular intervals and replacing it with fresh solution, which is calculated to compensate for the amount of dye lost by "drag-out".

By thus eliminating a portion of the impurities at regular intervals, the bath can be maintained in a constant state over a long period of time to give uniform dyeings. The frequency and the extent of partial renewal have to be determined on the basis of values derived from previous experience. Useful indications can be obtained by regular determinations of the dye concentration and the dyeing power. For instance, if the service life of a dye bath is expected to be 12 months without partial renewal, the rule of thumb can be applied that at constant aluminum throughput the state of the bath can be better stabilized for the period by replacing one twelfth of the volume every month.

The dyeing power can be determined as described in section 4.3. If an acceptable dyeing cannot be achieved even after a 50 % partial renewal, the bath must be renewed entirely. For weather fast dyeings the dyeing activity must be above 85 % at all times!

<sup>\*1)</sup> See section 9.5



# 5

## PREPARATION, MAINTENANCE AND SERVICE LIFE OF DYE BATHS

### 5.4 pH CORRECTION

The following reagents have proven to be most suitable for pH adjustment:

#### Acids

- Acetic acid: suitable for all pH regions, in particular the weakly acid region <sup>\*12)</sup>
- Formic acid: specially suitable for the pH region of 4 to 5
- Sulphuric acid for Sanodal Gold 4N

#### Alkalis

- Ammonia
- Caustic soda

The reagents are added to the bath in dilute form:

- Acetic acid and formic acid in at least 1:1 dilution
- Sulphuric acid, caustic soda, ammonia in at least 1:5 dilution

The best method is to check the pH of a bath sample in the laboratory and to calculate the amount of reagent necessary for pH adjustment, after which the dyeing behavior of the corrected sample is examined. The reagent is then added to the plant dye bath in the determined amount.

The pH of the dye bath should be checked every day.

### 5.5 BATH REPLACEMENT

Although Sanodure, Sanodye and Sanodal dye baths generally remain serviceable over a long period, from time to time they require partial renewal and eventually have to be replaced.

It is not possible to offer any general recommendations regarding the time scale or method of total bath replacement because the procedure to be followed depends a great deal on the finishing process conditions. The Sanodal dyeing system <sup>\*13)</sup> is an exception in that it defines the state of the dye bath which indicates that complete replacement is necessary.

### 5.6 MAINTENANCE AND STANDING TIME OF DYE BATHS

Sanodal, Sanodure and Sanodye dye baths can be kept in service for months or even years without deterioration in dyeing capacity, provided they are maintained with due care.

#### The following factors are crucial for lengthy service life:

- Dyeing tanks built of resistant materials <sup>\*14)</sup>
- Provision of covers to fit on the tanks when not in use
- Action to minimize the introduction of contaminants which inhibit dye adsorption, particularly aluminum, phosphates, silicates and sulfates <sup>\*15)</sup> by thorough rinsing before immersion in the dye bath
- Maintenance of the appropriate pH even when the dye bath is not in use
- Prevention of mold formation on the dye bath. With some dyes the addition of an antimicrobial product can inhibit mold formation for a long time.
- Use of deionized water for setting the baths <sup>\*16)</sup>

<sup>\*13)</sup> See section 6.3

<sup>\*14)</sup> See section 2.1

<sup>\*15)</sup> See section 3.5

<sup>\*16)</sup> See section 5.1

<sup>\*12)</sup> See section 4.1

## 5.7 DISPOSAL

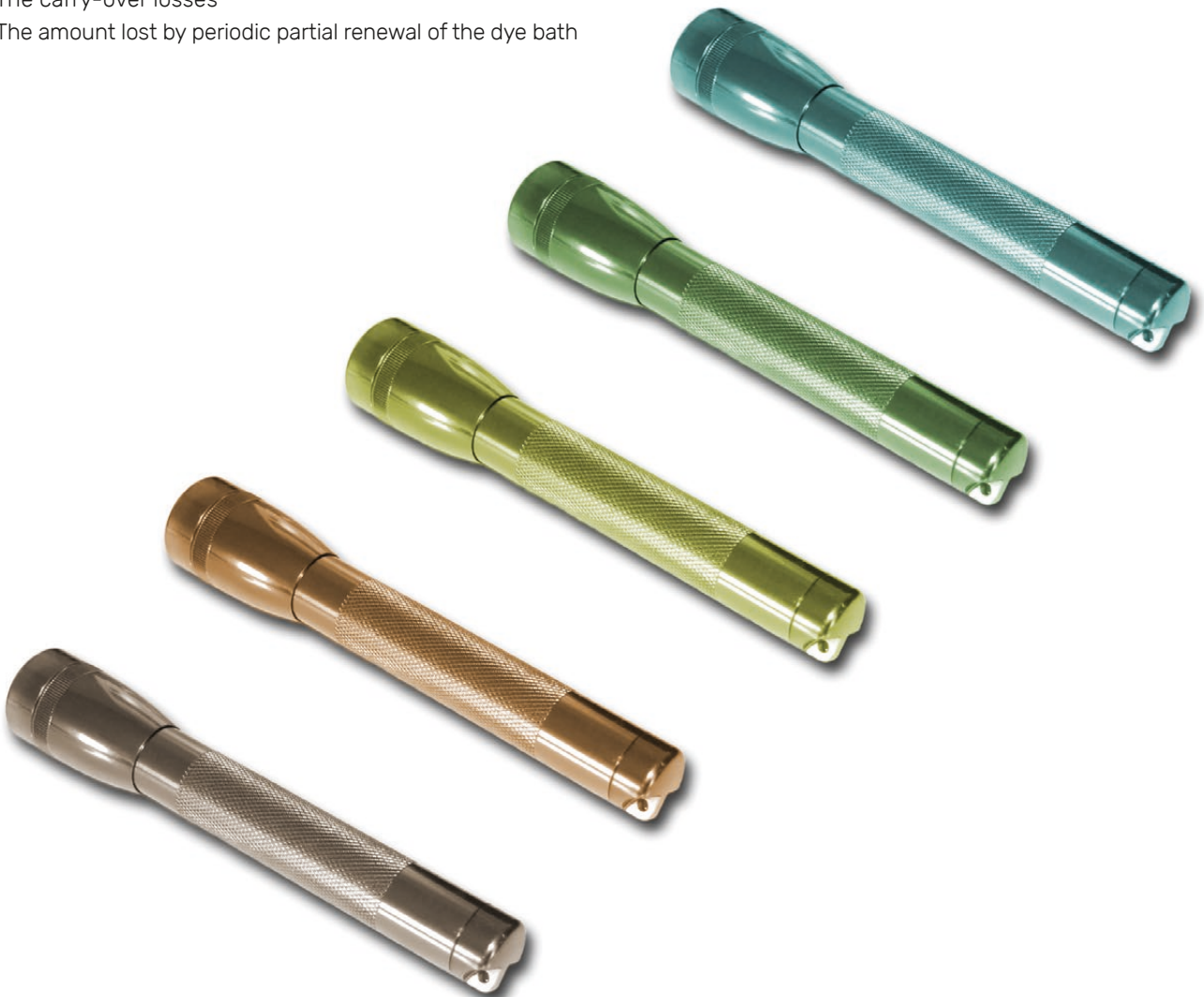
Spent dye baths and heavily colored rinsing water must be decolorized before being released to a waste water treatment plant or the communal drainage system by precipitation using Fe salts and Anodal® WT-1 liquid. Any disposal must be in line with your local government regulations. Please check with these authorities first.

## 5.8 RATE OF DYE CONSUMPTION

The overall consumption of dye per m<sup>2</sup> of dyed surface is made up of:

- The amount adsorbed in the coating
- The carry-over losses
- The amount lost by periodic partial renewal of the dye bath

Depending on the particular brand, the average rate of consumption ranges from 3 to 7 g/m<sup>2</sup>. In the case of the Black brands and Sanodal Gold 4N, the rate of consumption comes to 10–25 g/m<sup>2</sup> dyed surface area.



# 6

## SPECIAL CASES

### 6.1 DYE BLENDS

So far as possible, aluminum should not be dyed with mixtures of dyes. If the use of more than one dye is found to be unavoidable, as a rule only blends of not more than two dyes should be considered in the interest of good reproducibility.

Provided certain criteria are met, many Sanodal, Sanodure and Sanodye dyes can be mixed with one another, but not for coloring architectural aluminum. When working with such a mixture in a standing bath, after some time a shift of shade may be apparent which arises from one dye being adsorbed more rapidly than the other. It is therefore advisable to select elements for mixtures which are proven on the basis of previous experience.

Dyes with widely different pH values should not be dyed together. Brands with the "C" suffix should not be mixed with others without the suffix.

The sensitivity to aluminum and sulphate ions <sup>\*17)</sup> is another factor which has to be taken into account when selecting elements for mixed application, because the dyes differ in this respect.

### 6.2 DYEING OF CONVERSION COATINGS

Conversion coating on aluminum produced by chemical oxidation are dye-able with selected Sanodal, Sanodure and Sanodye dyes. However, depending on the method used to produce the coating it is not always possible to reach deeper shades. The abrasion resistance of the dyeings also leaves something to be desired.

### 6.3 DYEING ARCHITECTURAL ALUMINUM BY THE SANODAL PROCESS

For the production of light and weather resistant color finishes on building fitments, only dyes with appropriate excellent fastness properties are suitable. These are the Sanodal and some of the Sanodye grades. They have to be applied by the Sanodal system, which gives dyeings of high light and weather fastness by virtue of the following factors:

- Selected dyes whose color fastness has been proven by long term outdoor exposures
- The anodic coating has a average minimum thickness of 25 µm
- A minimum amount of dye for the specified intensity is adsorbed in the coating
- Sealing is carried out in nickel salt solutions

In order to obtain the high inherent light and weather fastness of these dyes the process has to be closely controlled.

The major factors requiring attention are:

- The dye content of the bath
- The relative dyeing power

Sanodal dyes can of course be employed for color finishes on aluminum products that are not destined for the construction industry, in which case it is not necessary to adhere strictly to the Sanodal process instructions.

\*17) See section 9.3

#### 6.4 OVERDYEING OF ELECTROLYTICALLY AND INTEGRALLY COLORED ALUMINUM

- Finishes produced by electrolytic methods with metallic salts or by
- Integral color anodizing <sup>\*18)</sup> can be overdyed

With Sanodal, Sanodure and Sanodye dyes, a range of pleasing and distinctive bronze and colorful shades can be produced.

On anodic coating of 25 µm minimum thickness, a combined process of this type will be found suitable for weather resistant architectural finishes, provided over dyeing is carried out in strict accordance with the Sanodal system.

#### 6.6 PRODUCTION OF MULTICOLORED ALUMINUM ARTICLES

Several techniques are available for producing multicolor finishes on anodized aluminum articles, the choice of technique being governed by the range of finishing equipment in the plant.

##### Resist printing process

In this process a film is applied to defined areas of the anodized surface by offset or screen printing to block (i. e. "resist") dyeing of the anodized coating.

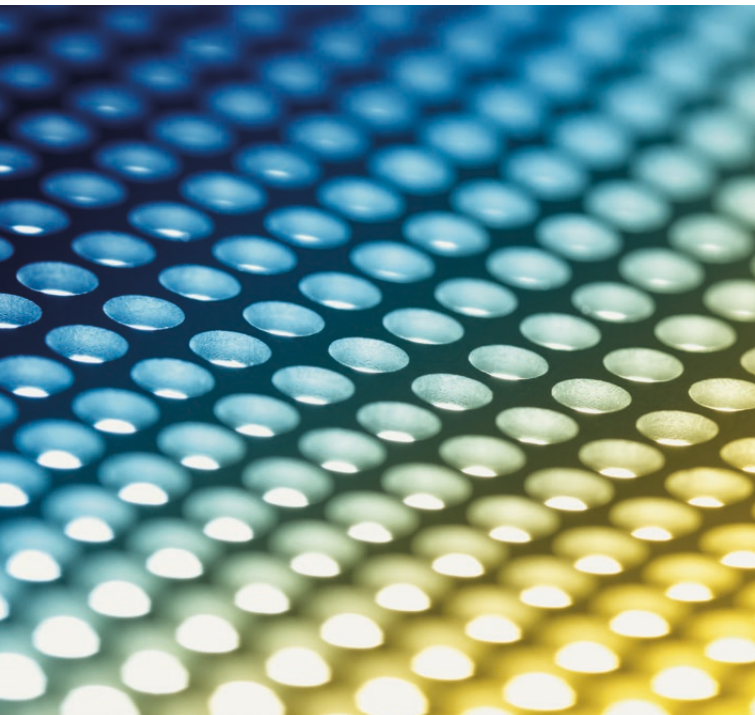
The unprotected areas are dyed with the water-soluble Sanodal, Sanodure and Sanodye dyes. Aluprint™ 3R Reducer is used for producing screen printed resists which are resistant to etching, over dyeing and subsequent anodizing.

##### Direct printing process

This process employs pastes which are printed on the anodic coating and color it directly. Applied by the screen printing process, the colored Aluprint 3R grades give deep local coloration. Once dried, colors printed with Aluprint 3R pastes are resistant to alkaline etching, over dyeing and subsequent anodizing. After sealing, the printed articles have to be cleared of residual color paste by rinsing with solvent.

##### Direct copying process

The anodic coating is coated with a photo-sensitized resist and exposed under a negative. The soft film on the nonimage areas washes off easily leaving the surface clear for dyeing with an aqueous Sanodal, Sanodure or Sanodye dye solution.



<sup>\*18)</sup> See section 1.3

# 7

## TREATMENT AFTER DYEING

### 7.1 RINSING AND INTERIM STORAGE

Newly dyed parts should be thoroughly rinsed to remove all loose dye adhering to the surface. Normally they are sealed immediately. Dyed parts that are to be overprinted are dried under controlled conditions at 20–50 °C/68–122 °F. In general, dyed parts should not be stored in water before sealing. The dyed surface should not be touched by hand before sealing.

### 7.2 DECOLORIZATION BY STRIPPING THE DYEING

If dyed parts are found to be off-shade when sampled prior to sealing, they can normally be stripped of dye or lightened in depth by treatment in nitric or sulphuric acid. These acids cause no serious damage to the anodic oxide coating, which can be redyed after the treatment. This method is also used for decolorizing in the manufacture of multicolored etched articles. The areas of the dyed surface which are to retain the previously applied color are coated with a resist, generally by offset printing, and the final multicolored design is built up step by step by subsequent stripping, redyeing in other colors, resist printing etc.

The table in section 9.4 gives information on the strip ability of the dyes with nitric and sulphuric acid.

After acid stripping the parts should be thoroughly rinsed. If the manufacturing process for multicolored nameplates involves stripping of dyed colors several times, it is advisable to dye at 20–40 °C/68–86 °F instead of in the normal 55–65 °C/131–149 °F region. The dyeings are then easier to strip <sup>\*19)</sup>. Dyeings produced at the lower temperatures should however be tested for satisfactory light fastness.

### 7.3 DECOLORIZATION BY STRIPPING THE DYED COATING

If the color fault is one that cannot be corrected by stripping and redyeing, or is only detected after sealing, or due to irregularities of the coating, then the anodic coating as well as the dyeing will have to be removed and the aluminum anodized anew before redyeing. It is easiest to remove the anodic coating by immersion in a caustic soda solution with the addition, for example, of Anodal EC-2 as a stone inhibitor. However, the underlying base metal is also attacked in this process, which may entail a new pretreatment to regain the original surface structure.

<sup>\*19)</sup> See section 3.1

# 8

## SEALING

Sealing closes the pores of the anodic oxide coating and fixes the dye deposited in the pores. The treatment is therefore an integral part of dyeing process. Unfortunately it is often found that sealing is not given sufficiently close attention in plant production. Correctly carried out, sealing – at its simplest treatment in boiling water – ensures that the dyeings will display the full inherent color fastness. Moreover it makes the parts resistant to finger-marks and to color and grease spots. Only after the anodized surface has been thoroughly sealed does it lose its tackiness to the touch. A point to be noted is that a small number of dyes undergo a slight shift of shade in the sealing solution. The shade reached at the end point of dyeing can be most nearly retained by rinsing the parts briefly on removal from the dye bath and sealing immediately after the rinse.

The sealing action is affected by the factors of time and temperature as well as the composition and pH of the baths. Depending on the sealing method used, the sealing time is 1–3 min/ $\mu\text{m}$ .

Pure water gives a very good seal. Additives to the sealing bath such as metal salts have a favorable effect on the dyeings and their fastness properties from several stand-points. However, dragged-in foreign substances such as sulphates and phosphates impair the sealing effect and promote bleeding of the dye into the solution.

The sealing bath should be set at pH 5.5 to 6. The pH adjustment is best obtained by adding dilute acetic acid or ammonia.

The following processes are normally used:

- Hot water sealing
- Steam sealing
- Nickel sealing
- Mid-temperature sealing
- Cold sealing

### 8.1 HOT WATER SEALING

Water sealing is the most widely used sealing method. Dyeings with the Sanodal, Sanodure and Sanodye dyes can be sealed in boiling water, though a certain amount of bleeding must be expected <sup>\*20)</sup>. On the metal surface an undesirable sealing smudge forms. Nowadays hot water sealing is carried out with the addition of a smudge suppressant such as Anodal SH-1 liquid.

### 8.2 STEAM SEALING

Sealing in steam is rarely used nowadays. For sealing purposes saturated steam at a temperature of 100 °C to 200 °C/212 °F to 392 °F is used. The sealing mechanism is the same as when sealing in hot water, and the sealing effect is very good. The sealing time is also 3 min/ $\mu\text{m}$  of coating thickness. With steam sealing the dyeings bleed or bleach out very little. Steam sealing is independent of the water quality; no impurities can be present which could impair the sealing effect.

<sup>\*20)</sup> See also section 8.8



# 8

## SEALING

### 8.3 NICKEL SALT SEALING

In industrial practice, sealing in nickel salt solutions is widely used. Compared with the more simple sealing in water, sealing with nickel salt solutions has a number of advantages. In nickel salt sealing, immediately after the beginning of the sealing process dissolved nickel salt precipitates in the outer region of the pores, thanks to which a sealing of the pores and blockage of the already-mentioned diffusion processes can be achieved after a short time. Sealing with nickel salt solutions is well suited for dyed anodic coatings.

The most widely used nickel salt is nickel acetate. Nickel sulphate sealing: This sealing method is not recommended because many of the dyes bleed out very heavily and hardly any nickel is deposited in the coating.

#### **Smudge from nickel sealing:**

When only nickel acetates are used for sealing, heavy smudge films are formed. However, these can be reduced by using Anodal ASL liq., which contain both a smudge prevention agent as well as a pH regulator. In any case, however, it is very recommendable to rinse off the aluminum pieces with water immediately after nickel sealing.

### 8.4 MID-TEMPERATURE SEALING

#### • **Water sealing**

With suitable chemicals such as Anodal SH-2 liquid, just as good a sealing quality can be reached at temperatures of 82–88 °C/180–190 °F as with hot water sealing. Anodal SH-2 liquid is added to sealing baths for colorless, color-anodized and electrolytically colored aluminum and prevents the formation of sealing smudge. Anodal SH-2 liquid can also be used for the smudge-free sealing of adsorptively dyed coatings or for combination dyeings with Sanodal, Sanodure and Sanodye dyes. In this case the two-stage sealing process is recommended, i. e. pre-sealing with Anodal ASL liquid and main sealing with water with the addition of Anodal SH-2 liquid.

#### • **Nickel salt sealing** (75–85 °C/167–185 °F)

Anodal MS-2 liquid

### 8.5 COLD SEALING

The anodic oxide coating is impregnated with an aqueous solution containing nickel fluoride. With a subsequent short hot water (>75 °C/167 °F) sealing, excellent resistance properties are achieved. For recommended products please ask our regional sales contact.

## 8.6 SEALING OF ADSORPTIVE ORGANIC DYED ALUMINUM

### Nickel acetate sealing

As already mentioned, organic dyed aluminum pieces are preferably sealed with nickel acetate in industrial practice, as bleeding of the dyes is minimal in this sealing medium and optimum weather fastness of the dyeings is obtained.

### Working method

One-stage process:

- 2.5 min/ $\mu\text{m}$
- 96–100 °C/205–212 °F in a solution of 15–20 g/l Anodal ASL liq.
- Rinse

Two-stage process:

- 30 s to 1 min/ $\mu\text{m}$  but for at least 5 min at 70 °C/158 °F in a Anodal ASL solution, then
- In deionized water with the addition of Anodal SH-1 liquid at 96–100 °C/205–212 °F for 2 min/ $\mu\text{m}$

## 8.7 MINIMIZING BLEEDING IN SEALING SOLUTIONS

Certain dyes tend to bleed during sealing, especially when water alone is used <sup>\*21)</sup>. The dyeings become correspondingly paler and the sealing bath is colored, although this is barely detectable.

Should several unfavorable factors come into play, the combined effect can even result in complete decolorization of the anodic coating.

By observing the following precautions, the difficulties noted above can be almost completely avoided:

- Dye for at least 5 min
- Prepare the dye bath with deionized water
- Rinse only briefly after dyeing and seal immediately
- Set the sealing solution with deionized water. Discard used solutions when the impurities reach a critical level
- Adjust the pH of the sealing solution to 5.5 with acetic or formic acid or ammonium acetate. Regular pH control and correction is necessary
- Seal at the boil
- Agitate the dyed parts immediately on immersion so that they are heated rapidly and evenly

## 8.8 AFTER-TREATMENT

After sealing the parts are rinsed and dried. If a powdery residue still exist on the surface it will be removed by gentle polishing.

<sup>\*21)</sup> See also section 9.5

## 9

# PROPERTIES OF THE DYES AND DYEINGS

The principal properties of the **Sanodal**, **Sanodure** and **Sanodye** dyes from Heubach and their dyeings are given in tabular form on this and the following pages.

- 9.1 Solubility
- 9.2 Characteristic data on pH and buffers
- 9.3 Sensitivity to ions
- 9.4 Strip ability of dyeings
- 9.5 Behavior of dyeings in sealing
- 9.6 Light fastness of dyeings
- 9.7 Heat stability of dyeings
- 9.8 Applications and features of the dyes
- 9.9 Physical, toxicological, ecological, storage and combustion data

## 9.1 SOLUBILITY

DYE	SOLUBILITY* IN WATER
	[g/l]
<b>SANODAL GOLD 4N</b>	>300
<b>SANODAL ORANGE 3LW LIQ.</b>	sol.
<b>SANODAL RED B3LW</b>	150
<b>SANODAL TURQUOISE PLW LIQ.</b>	sol.
<b>SANODAL GREEN 3LW</b>	100
<b>SANODAL BLACK 2LW</b>	50
<b>SANODAL DEEP BLACK H3LW</b>	misc.
<b>SANODAL DEEP BLACK HBL LIQ.</b>	sol.
<b>SANODAL DEEP BLACK MLW</b>	50
<b>SANODURE FAST GOLD L</b>	60
<b>SANODURE ORANGE G</b>	40
<b>SANODURE ORANGE RL</b>	40
<b>SANODURE FIERY RED ML</b>	75
<b>SANODURE BORDEAUX RL</b>	50
<b>SANODURE VIOLET CLW</b>	20
<b>SANODURE GREEN LWN</b>	40
<b>SANODURE BRONZE G</b>	15
<b>SANODURE BRONZE 2LW</b>	5
<b>SANODURE FAST BRONZE L</b>	100
<b>SANODURE BROWN GSL</b>	10
<b>SANODURE YELLOW BROWN 2G</b>	20
<b>SANODURE OLIVE BROWN 2R</b>	30
<b>SANODURE GREY HLN LIQ.</b>	misc.
<b>SANODURE GREY NL LIQ.</b>	misc.
<b>SANODURE BLACK CRO</b>	40
<b>SANODYE YELLOW 3GL</b>	100
<b>SANODYE ORANGE 2B</b>	7
<b>SANODYE GOLDEN ORANGE RLW</b>	100
<b>SANODYE BROWN R</b>	>300
<b>SANODYE RED GLW</b>	50
<b>SANODYE RED RLW</b>	100
<b>SANODYE MAGENTA LF</b>	85
<b>SANODYE VIOLET MRB NEW</b>	95
<b>SANODYE BLUE 2LW</b>	5
<b>SANODYE BLUE G</b>	3
<b>SANODYE BLACK OA</b>	20

\*at 20 °C/60 °F

## 9.2 CHARACTERISTIC DATA ON pH AND BUFFERS

DYE	CONCENTRATION [g/l]	INTRINSIC pH IN DEMINERALIZED WATER	OPTIMUM pH FOR DYEING	RECOMMENDED DYEING TEMPERATURE [°C/°F]	BUFFER
<b>SANODAL GOLD 4N</b>	10-30	3.5-4.5	4.0-5.0	40-55/104-131	-
<b>SANODAL ORANGE 3LW LIQ.</b>	0.05-3	5.0-9.0	5.0-6.0	25-60/77-140	S
<b>SANODAL RED B3LW</b>	0.05-5	4.0-8.0	5.0-6.0	25-60/77-140	S
<b>SANODAL TURQUOISE PLW LIQ.</b>	0.05-5	4.0-8.0	5.0-6.0	55-60/131-140	S*
<b>SANODAL GREEN 3LW</b>	0.05-3	5.0-9.0	5.0-6.0	25-60/77-140	S
<b>SANODAL BLACK 2LW</b>	0.1-10	3.5-4.5	4.0-4.8	25-60/77-140	-
<b>SANODAL DEEP BLACK H3LW</b>	0.1-10	3.0-7.0	5.0-6.0	25-60/77-140	S
<b>SANODAL DEEP BLACK HBL LIQ.</b>	0.1-10	5.0-9.0	5.0-6.0	25-60/77-140	S
<b>SANODAL DEEP BLACK MLW</b>	10	3.5-4.5	4.2-4.6	25-60/77-140	-
<b>SANODURE FAST GOLD L</b>	0.1-3	3.5-7.5	5.0-6.0	25-60/77-140	S
<b>SANODURE ORANGE G</b>	0.05-3	6.0-10.0	5.5-6.5	25-60/77-140	-
<b>SANODURE ORANGE RL</b>	0.05-3	7.5-12.5	5.5-6.5	25-60/77-140	-
<b>SANODURE FIERY RED ML</b>	0.05-5	3.0-5.0	5.0-6.0	25-60/77-140	S
<b>SANODURE BORDEAUX RL</b>	0.05-5	2.7-4.7	5.0-6.0	25-60/77-140	S
<b>SANODURE VIOLET CLW</b>	0.05-3	2.0-4.0	5.0-6.0	25-60/77-140	S
<b>SANODURE GREEN LWN</b>	0.05-3	5.0-9.0	5.5-6.0	25-60/77-140	S
<b>SANODURE BRONZE G</b>	0.05-3	1.9-3.9	5.0-6.0	25-60/77-140	S
<b>SANODURE BRONZE 2LW</b>	0.05-3	4.0-8.0	5.0-6.0	25-60/77-140	S
<b>SANODURE FAST BRONZE L</b>	0.05-3	8.5-12.5	5.0-6.0	25-60/77-140	S
<b>SANODURE BROWN GSL</b>	0.1-5	4.5-8.5	5.0-6.0	20-30/68-176	S
<b>SANODURE YELLOW BROWN 2G</b>	0.05-3	2.3-4.3	5.0-6.0	25-60/77-140	S
<b>SANODURE OLIVE BROWN 2R</b>	0.05-3	3.5-8.5	5.0-6.0	25-60/77-140	S
<b>SANODURE GREY HLN LIQ.</b>	0.1-5	6.0-10.0	5.5-6.0	20-60/68-140	S*
<b>SANODURE GREY NL LIQ.</b>	0.1-10	4.5-8.5	5.5-6.0	20-25/68-77	S*
<b>SANODURE BLACK CRO</b>	10-30	4.5-8.5	6.5-7.5	25-80/77-176	-
<b>SANODYE YELLOW 3GL</b>	0.05-4	4.9-8.5	5.0-6.0	25-60/77-140	S
<b>SANODYE ORANGE 2B</b>	0.5-5	9.8	9.0-11.0	25-65/77-149	S
<b>SANODYE GOLDEN ORANGE RLW</b>	0.05-3	5.5-10.5	5.5-6.5	25-60/77-140	-
<b>SANODYE BROWN R</b>	0.05-3	7.5-11.5	5.0-6.0	25-60/77-140	S
<b>SANODYE RED GLW</b>	0.05-4	5.5-9.5	5.0-6.0	25-60/77-140	S
<b>SANODYE RED RLW</b>	0.05-5	4.5-8.5	5.0-6.0	25-60/77-140	S
<b>SANODAL MAGENTA LF</b>	0.05-4	6.0-7.0	5.0-6.0	55-60/131-140	S
<b>SANODYE VIOLET MRB NEW</b>	2-5	5.8	5.0-7.0	55-65/131-149	S
<b>SANODYE BLUE 2LW</b>	0.05-3	1.5-7.0	5.0-6.0	25-60/77-140	A
<b>SANODYE BLUE G</b>	0.05-3	8.0-12.0	5.0-6.0	25-60/77-140	A
<b>SANODYE BLACK OA</b>	10	8.3	7.0-9.0	55-60/131-140	S

S 8.0g/l sodium acetate-trihydrate + 0.4ml/l acetic acid 100%

A 5.0g/l ammonium acetate + 0.5ml/l acetic acid 100%

\* Buffer addition necessary content has to be considered

## 9

# PROPERTIES OF THE DYES AND DYEINGS

## 9.3 SENSITIVITY TO IONS

DYE	CONCENTRATION [g/l]	SENSITIVITY TO			
		SULPHATE [g/l]	ALUMINUM [g/l]	SILICATE [g/l]	PHOSPHATE [g/l]
<b>SANODAL GOLD 4N</b>	30	>10	1.00	>0.20	>0.02
<b>SANODAL ORANGE 3LW LIQ.</b>	3	0.3	0.10	0.05	0.02
<b>SANODAL RED B3LW</b>	5	0.5	0.10*	0.05	0.01
<b>SANODAL TURQUOISE PLW LIQ.</b>	5	>4	0.05	0.10	0.05
<b>SANODAL GREEN 3LW</b>	2	0.4	0.10*	0.05	0.01
<b>SANODAL BLACK 2LW</b>	10	>4	0.20	0.20	>0.08
<b>SANODAL DEEP BLACK H3LW</b>	10	>4	0.20*	0.05	0.04
<b>SANODAL DEEP BLACK HBL LIQ.</b>	10	0.4	0.40	0.05	0.02
<b>SANODAL DEEP BLACK MLW</b>	10	2.2	0.05	>0.20	0.05
<b>SANODURE FAST GOLD L</b>	3	0.4	0.02*	0.05	0.04
<b>SANODURE ORANGE G</b>	3	2.2	0.02	0.10	0.04
<b>SANODURE ORANGE RL</b>	3	0.4	0.02*	>0.20	>0.08
<b>SANODURE FIERY RED ML</b>	5	>4	0.20	>0.20	0.06
<b>SANODURE BORDEAUX RL</b>	5	1.2	0.05	0.20	0.06
<b>SANODURE VIOLET CLW</b>	3	>4	0.15	0.10	0.03
<b>SANODURE GREEN LWN</b>	2	0.2	0.05	0.05	0.02
<b>SANODURE BRONZE G</b>	2	>4*	0.01	0.03	0.01
<b>SANODURE BRONZE 2LW</b>	2	0.2	0.02	0.04	0.01
<b>SANODURE FAST BRONZE L</b>	3	0.4	0.02*	0.01	0.01
<b>SANODURE BROWN GSL</b>	3	>4	0.01	>0.20	0.02
<b>SANODURE YELLOW BROWN 2G</b>	3	>4	0.01*	0.20	0.02
<b>SANODURE OLIVE BROWN 2R</b>	3	0.4	0.01*	>0.03	0.01
<b>SANODURE GREY HLN LIQ.</b>	3	0.2	0.1	0.05	0.02
<b>SANODURE GREY NL LIQ.</b>	3	0.8	0.01*	>0.20	0.01
<b>SANODURE BLACK CRO</b>	10	>4	0.40	0.01	0.01
<b>SANODYE YELLOW 3GL</b>	3	0.4*	>0.40	0.10	0.01
<b>SANODYE ORANGE 2B</b>	5	>4	>0.40	>0.20	>0.10
<b>SANODYE GOLDEN ORANGE RLW</b>	3	>4	0.15	0.20	0.03
<b>SANODYE BROWN R</b>	3	>4	0.01	>0.20	0.03
<b>SANODYE RED GLW</b>	4	>4	0.4	0.10	0.08
<b>SANODYE RED RLW</b>	3	>4	0.20*	0.10	0.04
<b>SANODAL MAGENTA LF</b>	4	1	0.10	0.05	0.01
<b>SANODYE VIOLET MRB NEW</b>	5	0.2	0.10	0.04	0.02
<b>SANODYE BLUE 2LW</b>	3	>4	0.01	0.05	0.02
<b>SANODYE BLUE G</b>	3	>4	0.02	>0.20	0.04
<b>SANODYE BLACK OA</b>	10	2	0.40	0.15	0.02

\* Precipitation concentration of ions in g/l when bath activity dropped to 80% according to Heubach test parameters



## 9.4 STRIP ABILITY

DYE	NITRIC ACID 30 %	SULPHURIC ACID 0.5 %	NITRIC ACID 10 % + POTASSIUM PERMANGANATE** 5 %
			[minutes*]
<b>SANODAL GOLD 4N</b>	5-10	>15	10-15
<b>SANODAL ORANGE 3LW LIQ.</b>	1	7	2
<b>SANODAL RED B3LW</b>	8	5	1
<b>SANODAL TURQUOISE PLW LIQ.</b>	>15	>15	1
<b>SANODAL GREEN 3LW</b>	2	10	1
<b>SANODAL BLACK 2LW</b>	2	12	1
<b>SANODAL DEEP BLACK H3LW</b>	>15	>15	1
<b>SANODAL DEEP BLACK HBL LIQ.</b>	>15	>15	1
<b>SANODAL DEEP BLACK MLW</b>	2	12	1
<b>SANODURE FAST GOLD L</b>	1	2	2
<b>SANODURE ORANGE G</b>	1	9	1
<b>SANODURE ORANGE RL</b>	>15	>15	1
<b>SANODURE FIERY RED ML</b>	2	8	1
<b>SANODURE BORDEAUX RL</b>	1	8	1
<b>SANODURE VIOLET CLW</b>	1	5	1
<b>SANODURE GREEN LWN</b>	8	>15	12
<b>SANODURE BRONZE G</b>	8	>15	1
<b>SANODURE BRONZE 2LW</b>	>15	>15	1
<b>SANODURE FAST BRONZE L</b>	15	3	3
<b>SANODURE BROWN GSL</b>	5	8	1
<b>SANODURE YELLOW BROWN 2G</b>	7	>15	1
<b>SANODURE OLIVE BROWN 2R</b>	>15	>15	2
<b>SANODURE GREY HLN LIQ.</b>	5	>15	4
<b>SANODURE GREY NL LIQ.</b>	>15	12	1
<b>SANODURE BLACK CRO</b>	>15	>15	5
<b>SANODYE YELLOW 3GL</b>	1	5	>15
<b>SANODYE ORANGE 2B</b>	>15	>15	>15
<b>SANODYE GOLDEN ORANGE RLW</b>	2	9	1
<b>SANODYE BROWN R</b>	>15	>15	10
<b>SANODYE RED GLW</b>	1	6	1
<b>SANODYE RED RLW</b>	1	6	1
<b>SANODAL MAGENTA LF</b>	5	>15	1
<b>SANODYE VIOLET MRB NEW</b>	5	>15	>15
<b>SANODYE BLUE 2LW</b>	6	>15	3
<b>SANODYE BLUE G</b>	6	>15	3
<b>SANODYE BLACK OA</b>	>15	>15	>15

The data apply to fresh, dark dyeings produced at 60 °C/140 °F on 12 µm coatings (Exception: Sanodure Grey NL at 25 °C/77 °F).

\* Stripping times in minutes at 25 °C/77 °F.

\*\* After the treatment in potassium permanganate, neutralization must be carried out for 1-5 minutes in a sodium bi-sulfite 5% solution.

# PROPERTIES OF THE DYES AND DYEINGS

## 9.5 BEHAVIOR OF DYEINGS DURING SEALING

DYE	BLEEDING
<b>SANODAL GOLD 4N</b>	nil
<b>SANODAL ORANGE 3LW LIQ.</b>	slight
<b>SANODAL RED B3LW</b>	heavy
<b>SANODAL TURQUOISE PLW LIQ.</b>	slight
<b>SANODAL GREEN 3LW</b>	slight
<b>SANODAL BLACK 2LW</b>	nil
<b>SANODAL DEEP BLACK H3LW</b>	heavy
<b>SANODAL DEEP BLACK HBL LIQ.</b>	slight
<b>SANODAL DEEP BLACK MLW</b>	nil
<b>SANODURE FAST GOLD L</b>	moderate
<b>SANODURE ORANGE G</b>	slight
<b>SANODURE ORANGE RL</b>	slight
<b>SANODURE FIERY RED ML</b>	moderate
<b>SANODURE BORDEAUX RL</b>	moderate
<b>SANODURE VIOLET CLW</b>	moderate
<b>SANODURE GREEN LWN</b>	heavy
<b>SANODURE BRONZE G</b>	slight
<b>SANODURE BRONZE 2LW</b>	slight
<b>SANODURE FAST BRONZE L</b>	moderate
<b>SANODURE BROWN GSL</b>	slight
<b>SANODURE YELLOW BROWN 2G</b>	slight
<b>SANODURE OLIVE BROWN 2R</b>	slight
<b>SANODURE GREY HLN LIQ.</b>	moderate
<b>SANODURE GREY NL LIQ.</b>	moderate
<b>SANODURE BLACK CRO</b>	moderate
<b>SANODYE YELLOW 3GL</b>	heavy
<b>SANODYE ORANGE 2B</b>	heavy
<b>SANODYE GOLDEN ORANGE RLW</b>	slight
<b>SANODYE BROWN R</b>	moderate
<b>SANODYE RED GLW</b>	moderate
<b>SANODYE RED RLW</b>	slight
<b>SANODYE MAGENTA LF</b>	nil
<b>SANODYE VIOLET MRB NEW</b>	moderate
<b>SANODYE BLUE 2LW</b>	heavy
<b>SANODYE BLUE G</b>	heavy
<b>SANODYE BLACK OA</b>	slight

*The data apply to standard coatings of 12–14 μm for a dyeing time of 15 minutes at 60 °C/140 °F and buffering according to table 9.2*

## 9.6 LIGHT FASTNESS

DYE	LIGHT FASTNESS <sup>1</sup>	CONCENTRATION	DYEINGS <sup>2</sup>	Dyeing temperature [°C/°F]	Dyeing time [min]
		[g/l]	pH		
<b>SANODAL GOLD 4N</b>	>9 <sup>2</sup>	30	4.5	45/113	0.5-20
<b>SANODAL ORANGE 3LW LIQ.</b>	>9	3	5.6B	25/77	30
<b>SANODAL RED B3LW</b>	>9	5	5.6B	60/140	30
<b>SANODAL TURQUOISE PLW LIQ.</b>	>9	5	5.6B	60/140	30
<b>SANODAL GREEN 3LW</b>	>9	3	5.6B	60/140	30
<b>SANODAL BLACK 2LW</b>	>9	10	4.5	60/140	30
<b>SANODAL DEEP BLACK H3LW</b>	>8 (12 μ); >10 (25 μ)	10	5.6B	60/140	30
<b>SANODAL DEEP BLACK HBL LIQ.</b>	>8 (12 μ); >10 (25 μ)	10	5.6B	60/140	30
<b>SANODAL DEEP BLACK MLW</b>	>9	10	4.5	60/140	30
<b>SANODURE FAST GOLD L</b>	7-8	3	5.6B	60/140	15
<b>SANODURE ORANGE G</b>	5-6	3	5.6	60/140	15
<b>SANODURE ORANGE RL</b>	5-6	3	5.6	60/140	15
<b>SANODURE FIERY RED ML</b>	6-7	5	5.6B	60/140	15
<b>SANODURE BORDEAUX RL</b>	6-7	5	5.6B	60/140	15
<b>SANODURE VIOLET CLW</b>	6-7	3	5.6B	60/140	15
<b>SANODURE GREEN LWN</b>	7-8	2	5.6B	60/140	15
<b>SANODURE BRONZE G</b>	6-7	2	5.6B	60/140	15
<b>SANODURE BRONZE 2LW</b>	7	2	5.6B	60/140	15
<b>SANODURE FAST BRONZE L</b>	7-8	3	5.6B	60/140	15
<b>SANODURE BROWN GSL</b>	6-7	3	5.6B	60/140	15
<b>SANODURE YELLOW BROWN 2G</b>	5-6	3	5.6B	60/140	15
<b>SANODURE OLIVE BROWN 2R</b>	6	3	5.6B	60/140	15
<b>SANODURE GREY HLN LIQ.</b>	7-8	3	5.6B	25/77	30
<b>SANODURE GREY NL LIQ.</b>	7-8	3	5.6B	25/77	30
<b>SANODURE BLACK CRO</b>	3-4 (12 μ); 7-8 (20 μ)	10	7	60/140	15
<b>SANODYE YELLOW 3GL</b>	>9	3	5.6B	60/140	20
<b>SANODYE ORANGE 2B</b>	5-6	5	5.6B	60/140	15
<b>SANODYE GOLDEN ORANGE RLW</b>	5-6	3	5.6B	60/140	15
<b>SANODYE BROWN R</b>	5-6	3	5.6B	60/140	15
<b>SANODYE RED GLW</b>	7	3	5.6B	60/140	15
<b>SANODYE RED RLW</b>	7	3	5.6B	60/140	15
<b>SANODAL MAGENTA LF</b>	9	4	5.6B	60/140	15
<b>SANODYE VIOLET MRB NEW</b>	3-4	5	5.6B	60/140	15
<b>SANODYE BLUE 2LW</b>	>9	3	5.6B	25/77	45
<b>SANODYE BLUE G</b>	>9	3	5.6B	35/95	45
<b>SANODYE BLACK OA</b>	>8	10	5.6B	60/140	20

1 Light fastness tested on standard coatings of 12-14 μm for Sanodure and Sanodye grades, and 21-23 μm for Sanodal dyes

2 Dyeing sealed with Anodal ASL liq.

\*\*B Dyeing in buffered medium

The dyeings were exposed to ISO 105-B02 (Weather-0 meter Atlas Ci35-A) and evaluated against the Blue Wool Scale according to ISO 2135.

With other coating thicknesses and dyeings and sealing conditions, other light fastness results may occur. For weather fast dyeings, only the Sanodal dyes applied by the Sanodal system are suitable.

## 9

# PROPERTIES OF THE DYES AND DYEINGS

## 9.7 HEAT STABILITY

DYE	CONCENTRATION [g/l]	HEAT			
		120 °C/248 °F 1500 h	150 °C/302 °F 1500 h	200 °C/392 °F 1h	200 °C/392 °F 10h
<b>SANODAL GOLD 4N</b>	30	5	5	5	5
<b>SANODAL ORANGE 3LW LIQ.</b>	3	-	2	5	4
<b>SANODAL RED B3LW</b>	5	4	2	5	4
<b>SANODAL TURQUOISE PLW LIQ.</b>	5	5	5	5	5
<b>SANODAL GREEN 3LW</b>	3	4	3	5	3
<b>SANODAL BLACK 2LW</b>	10	3	2	4	2
<b>SANODAL DEEP BLACK H3LW</b>	10	5	5	5	5
<b>SANODAL DEEP BLACK HBL LIQ.</b>	10	5	5	5	5
<b>SANODAL DEEP BLACK MLW</b>	10	3	2	4	2
<b>SANODURE FAST GOLD L</b>	3	5	4	5	5
<b>SANODURE ORANGE G</b>	3	5	4	5	5
<b>SANODURE ORANGE RL</b>	3	5	4	5	5
<b>SANODURE FIERY RED ML</b>	5	3	2	3	2
<b>SANODURE BORDEAUX RL</b>	5	2	2	3	2
<b>SANODURE VIOLET CLW</b>	3	4	3	4	3
<b>SANODURE GREEN LWN</b>	2	4	2	2	1
<b>SANODURE BRONZE G</b>	2	3	2	5	4
<b>SANODURE BRONZE 2LW</b>	2	2	1	3	2
<b>SANODURE FAST BRONZE L</b>	3	5	3	5	5
<b>SANODURE BROWN GSL</b>	3	3	2	5	4
<b>SANODURE YELLOW BROWN 2G</b>	3	3	2	5	4
<b>SANODURE OLIVE BROWN 2R</b>	3	3	2	5	2
<b>SANODURE GREY HLN LIQ.</b>	3	-	2	5	3
<b>SANODURE GREY NL LIQ.</b>	3	2	2	3	2
<b>SANODURE BLACK CRO</b>	10	-	1	3	1
<b>SANODYE YELLOW 3GL</b>	3	5	5	5	5
<b>SANODYE ORANGE 2B</b>	5	5	5	5	4
<b>SANODYE GOLDEN ORANGE RLW</b>	3	5	5	5	5
<b>SANODYE BROWN R</b>	3	3	2	4	3
<b>SANODYE RED GLW</b>	3	5	4	5	5
<b>SANODYE RED RLW</b>	3	5	4	5	5
<b>SANODAL MAGENTA LF</b>	4	4-5	3-4	5	4-5
<b>SANODYE VIOLET MRB NEW</b>	5	3	2	4	3
<b>SANODYE BLUE 2LW</b>	3	5	5	5	5
<b>SANODYE BLUE G</b>	3	5	5	5	5
<b>SANODYE BLACK OA</b>	10	2	1	4	2

Ratings: 5 Heat stable (no visible change)  
4 Slight change  
3 Moderate change  
2 Marked change  
1 Dyeing destroyed

DC standard 12–13µm, Dyeing for 15 min at 60 °C/140 °F  
Sanodure Grey NL at 25 °C/77 °F  
Sanodal Gold 4N at 45 °C/113 °F  
pH and buffering see table 9.2  
Sealing with 5 g/l Anodal ASL liq.  
40 min 98 °C/208 °F

## 9.8 APPLICATIONS AND FEATURES OF THE DYES

DYE	APPLICATIONS	REMARKS
<b>SANODAL GOLD 4N</b>	For inorganic gold shades including pale dyeing: light-fast; high heat stability	Optimum dyeing temperature 35–45°C/95–113°F. Set bath with deionized water; dye baths are light sensitive
<b>SANODAL ORANGE 3LW LIQ</b>	For high-strength orange shades	Can be shaded with Sanodal Yellow S-3LW. For weather resistant parts, dye at room temperature
<b>SANODAL RED B3LW</b>	For neutral red shades for kitchen wares	Very high light and weather fastness
<b>SANODAL TURQUOISE PLW LIQ</b>	For high-strength turquoise shades	For weather resistant parts, anodic coating must be at least 25 µm; shadable with Sanodye Yellow 3GL
<b>SANODAL GREEN 3LW</b>	Multipurpose green dye	Calcium-sensitive; set bath with deionized water only
<b>SANODAL BLACK 2LW</b>	For bluish black shades	Bluish-green tones in pale dyeings
<b>SANODAL DEEP BLACK H3LW</b>	Multipurpose dye; slightly reddish shade in artificial light	Deep black shades even on coatings of 10 µm
<b>SANODAL DEEP BLACK HBL LIQ</b>	Multipurpose dye for neutral black tones	Very high heat stability; deep black shades even on coatings of 10 µm
<b>SANODAL DEEP BLACK MLW</b>	Shaded multipurpose dye for warm black shades	Do not use for gray tones
<b>SANODURE FAST GOLD L</b>	For jewelery	Can be shaded with Sanodure Fast Bronze L from yellow to red-gold
<b>SANODURE ORANGE G</b>	Multipurpose dye, also for jewelery	Very economical; dissolve dye hot before adding to dye bath
<b>SANODURE ORANGE RL</b>	For jewellery; yellower shade than Sanodure Orange G	More than 1g/l should not be buffered
<b>SANODURE FIERY RED ML</b>	For vivid red shades and nameplate finishes	Can be shaded with Sanodye Red RLW or Sanodure Bordeaux RL
<b>SANODURE BORDEAUX RL</b>	For bluish red shaded	Can be shaded with Sanodye Red RLW
<b>SANODURE VIOLET CLW</b>	Multipurpose dye	Rapid adsorption rate

*The Sanodal dyes, as opposed to the aluminum dyes, are specially suitable for exterior architectural applications.*



## 9

# PROPERTIES OF THE DYES AND DYEINGS

## 9.8 APPLICATIONS AND FEATURES OF THE DYES

DYE	APPLICATIONS	REMARKS
<b>SANODURE GREEN LWN</b>	Multipurpose dye	Cold dyeing is best for bath stability; pH not lower than 5.5
<b>SANODURE BRONZE G</b>	For reddish bronze shades	Limited light fastness
<b>SANODURE BRONZE 2LW</b>	For yellowish bronze shades	Cold dyeing is best for bath stability; pH not lower than 5.5
<b>SANODURE FAST BRONZE L</b>	For jewelery; reddish gold shades	Can be shaded with Sanodure Fast Gold L from red to yellow-gold
<b>SANODURE BROWN GSL</b>	For neutral brown shades	Sensitive to aluminum ions
<b>SANODURE YELLOW BROWN 2G</b>	Multipurpose dye	Can be shaded with Sanodure Bordeaux RL or Golden Orange RLW
<b>SANODURE OLIVE BROWN 2R</b>	For military equipment	Sealing with Anodal SH-1 gives olive green, Anodal ASL sealing gives olive brown shades
<b>SANODURE GREY HLN LIQ</b>	Multipurpose neutral gray dye	Very sensitive to sulphate
<b>SANODURE GREY NL LIQ</b>	For brownish gray shades	Dye at room temperature only; can be shaded with Sanodal Black GL Paste
<b>SANODURE BLACK CRO</b>	Specialty dye for continuous dyeing	Limited light fastness
<b>SANODYE YELLOW 3GL</b>	For greenish yellow shades	Very high light fastness
<b>SANODYE GOLDEN ORANGE RLW</b>	Multipurpose dye, also for gold shades	Can be shaded with Sanodye Red GLW
<b>SANODYE RED GLW</b>	Multipurpose dye for yellowish red shades	Also for shading gold tones
<b>SANODYE RED RLW</b>	For very deep red shades	Can be shaded with Sanodure Bordeaux RL
<b>SANODYE MAGENTA LF</b>	Multipurpose dye for bluish red shades	Good light and weather fastness
<b>SANODYE BLUE 2LW</b>	Multipurpose blue dye, slightly greener than Sanodye Blue G	For weather resistant parts, dye at max. 35 °C/95 °F
<b>SANODYE BLUE G</b>	Multipurpose blue dye	For weather resistant parts, dye at max. 40 °C/104 °F
<b>SANODYE BROWN R</b>	For reddish brown shades	Dissolve dye hot before adding to dye bath
<b>SANODYE BLACK OA</b>	N.A.	N.A.

## 9.9 PHYSICAL, TOXICOLOGICAL, ECOLOGICAL, STORAGE AND COMBUSTION DATA

These data are given in the Safety Data Sheets for the individual products. The Safety Data Sheets are available on request.



# 10

## CHEMICALS FOR ANODIZING, DYEING AND SEALING

These are the globally available Heubach chemicals for aluminum finishing. Further products are available depending on the sales region. Please contact your local representative for information about regional products.

### ETCHING

- **Anodal EC-2 liquid**

Silicate and chlorate-free, liquid complexing agent for preparing E6 long-term etching baths for aluminum and its alloys. Specially suitable for alloys containing zinc.

### ANODIZING

- **Anodal EE liquid**

Enables hard anodizing with a normal sulphuric acid solution, without expensive cooling and high-voltage equipment.

- **Anodal SUAC liquid**

An electrolyte for the integral color anodizing of aluminum.

### ELECTROLYTIC COLORING

- **Anodal color S-2 liquid**

Metal-free, highly efficient stabilizer for electrolytic tin coloring baths, for improving bath stability, color distribution and shade depth.

### SEALING

- **Anodal SH-1 liquid**

Multipurpose smudge suppressant for hot water sealing at boiling temperature.

- **Anodal SH-2 liquid**

Multipurpose smudge suppressant for mid temperature (82–90 °C/180–194 °F) sealing.

- **Anodal MS-2 liquid**

Nickel acetate for water sealing at 75–85 °C/167–185 °F.

- **Anodal ASL liquid**

Nickel acetate preparation for high-quality, smudge-free hot nickel sealing. This product is specially recommended with organic-dyed coatings as well as in the case of inferior water quality.

- **Anodal WL spec.**

Sealing additive used on its own or in combination with other sealing additives to improve haptic properties and scratch resistance of anodized surfaces.

### WASTE WATER TREATMENT

- **Anodal WT-1**

Flocking additive for waste water treatment; removal of dissolved dyestuff.



# 11

## DYEING FAULTS, THEIR CAUSES AND PREVENTION

When faults occur in the color finishing of aluminum leading to rejection of the work, there is a widespread tendency in the industry to blame the dyeing process or even the dyes, without looking further into the cause of the trouble. Experience has demonstrated that very often undetected or undetectable deviations in the pretreatment of the metal are responsible for color faults.

The following information should help to dispel this misconception by indicating possible causes of color faults and outlining suitable action for their prevention.

The term "color faults" is understood here to mean deviations from a quality standard which are visible to the unaided eye and are due to errors in the preliminary surface treatment or dyeing that are not visible until after completion of dyeing. The relationship between the process conditions and the color of the finish is not considered except in so far as it can be used to prevent or correct color faults. Similarly lack of color constancy and physical or color imperfections such as defects on the metal surface or self-color in the anodic coating which are detectable prior to dyeing, are left out of account.

The following tables cover the subject under three column headings:

- Description of color faults
- Possible cause or causes
- Preventive or corrective action



# 11

# DYEING FAULTS, THEIR CAUSES AND PREVENTION

## A. COLOR DIFFERENCES FROM BATCH TO BATCH

TYPE OF COLOR FAULT	POSSIBLE CAUSES	PREVENTIVE ACTION
Slow decrease in depth (over days or weeks)	<p><b>Decline in dyeing capacity due to:</b></p> <ul style="list-style-type: none"> <li>• Drop in dye concentration through consumption</li> <li>• Accumulation of deactivating contaminants in dye bath</li> <li>• Chemical decomposition of dye through contact with nonresistant metal parts</li> <li>• Slow increase in pH</li> </ul>	<ul style="list-style-type: none"> <li>• Add dye to correct</li> <li>• Prevent entrainment by thorough rinsing and deficiency by avoiding dripping from other solutions</li> <li>• Extend dyeing time</li> <li>• Increase dye concentration above the initial value</li> <li>• Partial or full renewal of dye bath</li> <li>• Check tank and fittings for possible points of contact and insulate these points</li> <li>• Correct pH, buffer the bath</li> </ul>
Depth differences	<p><b>Variations in dye absorptive capacity of anodic coating due to:</b></p> <ul style="list-style-type: none"> <li>• Inconstant anodizing conditions</li> <li>• Presence of different alloys</li> <li>• Different time lag between anodizing and dyeing (acid dip, carryover into rinsing bath, retention time in water and air)</li> <li>• Uneven activation in the acid dip</li> <li>• Different degrees of bleeding in the sealing bath</li> <li>• Fluctuation in dye bath pH</li> </ul>	<ul style="list-style-type: none"> <li>• Keep anodizing conditions constant (current density, time, temperature)</li> <li>• Adjust anodizing and dyeing parameters to the alloys present</li> <li>• Keep the time interval constant</li> <li>• Do not suspend in anodizing acid without current, rinse immediately afterwards</li> <li>• Do not store in water</li> <li>• Treat further without a break so far as possible</li> <li>• Level out dye absorptive capacity by brief activation in acid and a neutralizing rinse</li> <li>• Keep activation time constant</li> <li>• Equalize or minimize losses from bleeding by:               <ul style="list-style-type: none"> <li>- Sealing in Anodal ASL</li> <li>- Dye at higher temperature or for longer time at lower dye concentration</li> <li>- Use deionized water for sealing</li> <li>- Immerse at highest practicable sealing temperature</li> <li>- Keep sealing pH constant, buffer bath</li> </ul> </li> <li>• Buffer dyeing solution where recommended</li> </ul>
Over-heavy dyeing at beginning of production run	Increase in the anodizing temperature	<ul style="list-style-type: none"> <li>• Do not dye the first anodizing batches</li> </ul>
Changes of shade	<p>Uneven depletion of elements in dye blends</p> <p>Chemical instability of the dye in solution</p>	<ul style="list-style-type: none"> <li>• Correct concentration of the component involved</li> <li>• Use single dyes whenever possible</li> <li>• Employ combinations of dyes with similar dyeing rates</li> <li>• Select dyes with higher stability in solution</li> <li>• Optimize dyeing conditions (lower temperature, more suitable pH, buffer)</li> <li>• Renew dye solution at frequent intervals</li> </ul>



## B. COLOR DIFFERENCES IN THE SAME BATCH

TYPE OF COLOR FAULT	POSSIBLE CAUSES	PREVENTIVE ACTION
Color differences from part to part	Irregular current supply due to uneven contacts on the auxiliary anode frame	<ul style="list-style-type: none"> <li>• Create uniformly good contact points</li> <li>• Clean the contact points</li> </ul>
Gradations of shade on marginal areas with darker edges	<p data-bbox="560 636 995 658">Presence of different alloys</p> <p data-bbox="560 730 995 801">Irregularities in current density and heat distribution (heat accumulation at edges) in anodizing</p>	<ul style="list-style-type: none"> <li>• Dye only alloys of the same type in a given batch</li> <li>• Improve the electrode geometry</li> <li>• Intensify admixture of electrolyte</li> <li>• Reduce current density</li> <li>• Intensify cooling, choose lower anodizing temperature</li> <li>• Reduce aluminum content of electrolyte</li> <li>• Select lower dyeing temperature and longer dyeing time</li> </ul>
Lower areas of the part darker	Differences in immersion time in the dye solution between upper and lower areas due to method of immersion	<ul style="list-style-type: none"> <li>• Extend total dyeing time to more than 10 min and adjust other parameters, i. e. reduce temperature and concentration</li> <li>• Accelerate immersion</li> </ul>
Horizontal color fronts in upper region of the part with striped, often wavy shaded spots	A film, usually oil containing, adheres to the work when lifted clear of the bath	<ul style="list-style-type: none"> <li>• Remove film from the bath (clarify by filtration, absorb on absorbent material, collect with a blade and skim off)</li> <li>• Intensify bath agitation</li> </ul>



# 11

## DYEING FAULTS, THEIR CAUSES AND PREVENTION

### C. COLOR DIFFERENCES IN THE SAME PART (NONUNIFORMITY, COLORED SPOTS)

TYPE OF COLOR FAULT	POSSIBLE CAUSES	PREVENTIVE ACTION
Large cloudy areas covering the single workpiece	Anodizing temperature not sufficiently uniform (heat convection streaks)	<ul style="list-style-type: none"> <li>• Intensify bath agitation</li> <li>• Reduce current density</li> </ul>
Pale spots	<p>Insufficient degreasing action</p> <p>Spray of air agitated anodizing bath</p> <p>Oily impurities in anodizing or dye bath</p> <p>Inadequate rinsing</p> <p>Uneven wetting of the parts in the dye bath</p> <p>Hydrolyzed aluminum not eliminated by rinsing</p> <p>Local over-heating in polishing (polishing clouds)</p>	<ul style="list-style-type: none"> <li>• More thorough degreasing</li> <li>• Add wetting agent to anodizing bath to form foam cushion</li> <li>• Keep bath clear of impurities (oil-free compressed air) or remove if present</li> <li>• More thorough rinsing</li> <li>• Immerse in the dye bath in wet state only</li> <li>• Short acid treatment (activation) and rinsing prior to dyeing</li> <li>• Intensify mixing of bath components, or preferably agitate the parts during immersion and in the first dyeing phase</li> <li>• Add leveling agent to the bath</li> <li>• Rinse thoroughly immediately after anodizing</li> <li>• Follow rinsing with acid treatment (activation) or acid rinsing (pH below 2) with a subsequent neutralizing rinse</li> <li>• Brief anodizing treatment, etching</li> </ul>
Numerous pale pointed spots, especially in pale dyeings	Gas bubbles at the pore openings inhibiting dye penetration	<ul style="list-style-type: none"> <li>• Immerse parts in wet state free from gas bubbles</li> <li>• Agitate parts on immersion until no further gas bubbles rise to the surface</li> <li>• Dye at room temperature</li> </ul>
Pale spots at cavities and depressions	Occluded gas bubbles interfering with the anodizing or dyeing process	<ul style="list-style-type: none"> <li>• Intensify agitation of the parts or the solution to detach bubbles as rapidly as possible</li> <li>• Dye at room temperature</li> </ul>
Pale spots in cavities (angles) or pale stripes running from cavities to edges	Deposits or exudations of anodizing acid which inhibit dyeing	<ul style="list-style-type: none"> <li>• Plan construction and suspension of parts to facilitate draining of acid, (e. g. not completely closed selvages, drainages holes)</li> <li>• Rinse thoroughly immediately after anodizing</li> <li>• After rinsing, neutralize, activate (acid dip), rinse</li> </ul>
Dark spots in cavities (angles) or dark stripes running from cavities, dark stripes on horizontal edges, dark, drop-shaped points	Drip deposits and outflows from dye solutions (spots showing on drying can be partially cleared by wiping), over-heavy dyeing due to local continuation of dyeing process by superficially attached dye solution	<ul style="list-style-type: none"> <li>• After dyeing do not leave parts unrinsed, rinse at once</li> <li>• Reduce dyeing temperature and extend dyeing time</li> <li>• Facilitate drainage of dye solution</li> </ul>
Dark spots	Undissolved, retained dye particles	<ul style="list-style-type: none"> <li>• Do not add dry powder dye, prepare an aqueous concentrate (dissolve or disperse) and add dye through a fine gauze screen if available</li> <li>• Boil up dye bath with agitation</li> <li>• Clarify dye bath by filtration</li> </ul>

## D. VISIBLE DEFICIENCIES IN COLOUR QUALITY

TYPE OF COLOR FAULT	POSSIBLE CAUSES	PREVENTIVE ACTION
Dull to chalky dyeing, often not resistant to wiping	Over-soft anodic coating, especially pronounced in marginal areas, owing to inadequate anodizing	<ul style="list-style-type: none"> <li>• Reduce anodizing temperature, time current, density, acid-, and aluminum concentration, intensify motion of the electrolyte</li> </ul>
	Over-heavy activation, perhaps combined with unsatisfactory anodizing	<ul style="list-style-type: none"> <li>• Shorten retention time in acid bath</li> </ul>
	Current-free suspension in anodizing electrolyte or in unrinsed state	<ul style="list-style-type: none"> <li>• After switching off current, lift the parts at once and rinse</li> </ul>
	Coating attacked owing to unduly low bath pH	<ul style="list-style-type: none"> <li>• Increase the pH to at least 4</li> </ul>
Opaque, dull to bronzing dyeing, removable by wiping	Superficial pigmentation due to premature precipitation of dye, frequently caused by excess of dissolved or hydrolyzed aluminum	<ul style="list-style-type: none"> <li>• Increase dye bath pH to at least 4</li> <li>• Acid dip (activation) prior to dyeing to dissolve and clear aluminum</li> </ul>

# 12 GENERAL NOTES

## 12.1 PATENT PROTECTION

It should be noted that certain brightening, anodizing and sealing processes are protected by patents.

## 12.2 LITERATURE

For further information on the anodic oxidation of aluminum the following publications may be consulted:

1. *The Surface Treatment and Finishing of Aluminium and its Alloys*, P. G. Sheasby – R. Pinner, Vols. 1&2, 6<sup>th</sup> Edition, ASM International-Finishing Publications Ltd.
2. *Oberflächenbehandlung von Aluminium*, T. W. Jelinek, Eugen G. Leuze Verlag
3. *The Technology of Anodizing Aluminium*, A. W. Brace
4. *Die Praxis der anodischen Oxidation des Aluminiums*, W. Hubner – Th. Speiser, Aluminium-Verlag GmbH
5. *Die Oberflächenbehandlung von Aluminium*, Simon Wernick – Robert Pinner – Emil Zurbrügg, Eugen G. Leuze Verlag
6. *Aluminium Taschenbuch Vols. 1-3*, Aluminium-Verlag
7. *The Metallurgy & Anodizing Aluminum* Connecting Science to Practice

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