

FOR LIGHT-FAST AND
WEATHER-FAST DYEING
SANODAL®



FOR LIGHT-FAST AND WEATHER-FAST DYEING **SANODAL® SYSTEM**

When in 1886 the electrolytic extraction of aluminum was successfully carried out for the first time, this new metal began an undreamed-of triumphant advance which still continues. This still highly modern material is lightweight, resistant, corrosion proof, stable to heat and frost, and reusable. Aluminum can be forged, rolled, pressed and cast. In addition, aluminum has a very special property – its anodic coating can be dyed with organic and inorganic dyestuffs, without losing the magic of the metallic gloss.



In architecture, not only form but also color plays a very important role. The well-known electrolytic coloring processes, which can produce a number of hues limited to bronze, copper, grey and black, cannot fully satisfy architectural desires for color.

With the Sanodal system developed by Heubach, a whole range of light-fast and weather-fast shades can be produced. The Sanodal system is based on the proven principle of adsorptive dyeing of anodically produced oxide coatings with organic dyes by immersion or the spraying method.

By a selective use of dyes, strict quality control and suitable application processes, dyeing produced by the Sanodal system can meet exterior architectural requirements. The working methods described here, which can be carried out with simple means, permit uninterrupted process monitoring and offer the aluminum finisher a high level of operating safety, making it possible to reliably produce highest quality dyeings which meet the requirements of exterior architecture.

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1 WORKING METHODS AND EXPLANATIONS

Outstanding light and weather fastness of dyeings with organic and inorganic dyes on aluminum architectural elements will only be achieved when the application conditions and tolerance limits prescribed here are exactly observed in:

- Anodizing
- Dyeing
- Sealing

For the aftertreatment, the working methods normally prescribed for exterior architecture apply.



1.1 MATERIALS, PRETREATMENT

All normal aluminum alloys suitable for architectural uses and for anodizing (»anodizing quality«) can be dyed by the Sanodal system. This applies both to roller and press-produced alloys.

Alloys of the following type (ISO standard) are mostly used:

- | | |
|--------------|--|
| AlMg 1-3 | Primarily rolled products such as sheet, coils, etc. |
| AlMgSi 0.5-1 | Mostly extrusion-moulded sections |

Aluminum construction elements are pretreated by the usual methods.

1.2 ANODIZING, RINSING

ANODIZING CONDITIONS, DC METHOD

Free sulphuric acid	180–220 g/l, preferably 200 g/l
Aluminum content	5–15 g/l
Acid additions	none
Electric current	Current density: 1.5 A/dm ² ± 0.3 A/dm ² Voltage: approx. 15 V, resulting from current density
Temperature	19 °C ± 1 °C
Duration	50–70 min, depending on current density
Anodic coating thickness	average minimum thickness 25 µm; in no case less than 80 % of 25 µm = 20 µm

The prescribed minimum thickness of 20 µm is designated in a number of national standards and in the Qualanod®² guidelines. Fault-free dyeings presuppose that the anodizing conditions according to our working methods are observed within narrow limits.

INFLUENCE OF ANODIZING FACTORS

ANODIZING FACTORS	DEVIATION FROM PRESCRIBED WORKING METHOD	HARDNESS, CORROSION RESISTANCE	DYE UPTAKE CAPACITY
Sulphuric acid concentration	higher	lower	higher
	lower	higher	lower
Aluminum content	higher	–	nonuniformity of surface
	lower	slightly lower	slightly higher
Oxalic acid or similar addition	with addition	higher	lower
Current density (for same anodic oxide coating thickness)	higher	higher*	lower
	lower	lower	higher
Temperature	higher	lower	higher
	lower	higher	lower
	localized temperature differences	–	uneven dyeings
Time (coating thickness)	longer	higher	higher
	shorter	lower	lower

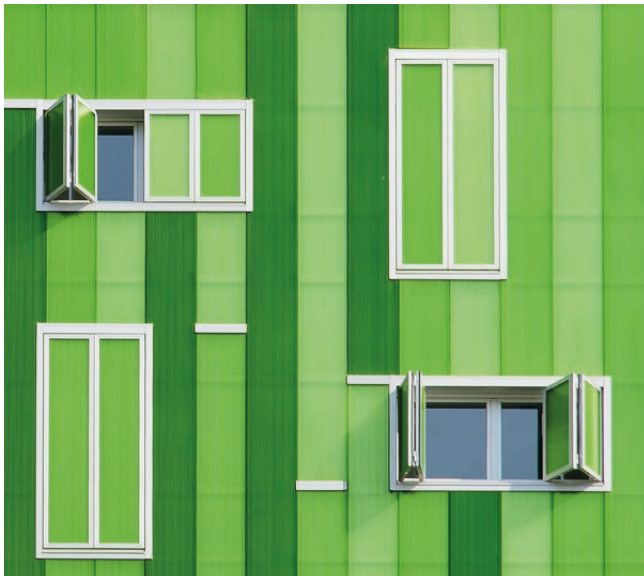
* The dissipation of heat can be a problem.

RINSING AFTER ANODIZING

After anodizing, the aluminum elements are rinsed for several minutes in cold running tap water. The rinsing water must be cold, as higher temperatures can cause undesirable effects later in the sealing operation.

Optimum results are obtained, for example, with multi-stage cascade rinsing. Spraying off the elements before the first rinsing tank has also proved to be very effective.

It is important that the anodizing acid has completely run off before rinsing, and that the rinsing water reaches all parts of the element so that any residual sulphuric acid and/or aluminum ions remaining on the piece are removed.



Above all, the rinsing should be thorough so as to prevent aluminum and sulfate ions, which can be very destructive in the dye bath, from being dragged in. Therefore the aluminum elements should be positioned for anodizing in such a way that the acid can freely run off all parts of the section when it is removed and not remain trapped in any horizontal cavities.

To control the rinsing operation, the degree of neutrality of the anodic coating can be determined (see section 2.1). Also, any contamination of the dye bath can be further reduced by using deionized water in the last rinsing step.

Anodized parts should not be left to stand for a long time before dyeing. After a storage time of only 24 hours in a moist atmosphere, the dye adsorption capacity becomes noticeably lower, whereas storage for up to 3 days in a dry place only slightly impairs the dye adsorptivity. After storage an activation with dilute nitric acid (~ 8-10 %) should always be carried out.

1.3 DYEING

As a rule, according to the Sanodal system, dyes are applied by the immersion method. However it is also possible to apply the aqueous dye solution by the spraying method, which offers certain advantages: for example, the volume of the dye solution can be reduced by a factor of about ten. The disadvantage is that the dye bath must be reinforced more often due to the smaller dye volume.

For each of the dyes suitable for the Sanodal system technical information bulletins are available which contain more details about the specific general properties and application conditions for the particular dye of interest.

DYEING CONDITIONS

DYE	AMOUNT [g/l]	pH	BUFFER	DYEING TEMP. [°C]	DYEING TIME [min.]
SANODYE® YELLOW 3GL	3	5.5-6.0	S	55-60	30-40
SANODAL GOLD 4N	10-30	4.2-4.7	*	35-50	0.5-20
SANODAL ORANGE 3LW LIQUID	3	5.5-6.0	S	25-35	45-60
SANODAL RED B3LW	5	5.5-6.0	S	55-60	30-40
SANODYE BLUE G	3	5.5-6.0	A	30-40	45-60
SANODYE BLUE 2LW	3	5.5-6.0	A	25-35	45-60
SANODAL TURQUOISE PLW LIQUID	5	5.5-6.0	S	55-60	45-60
SANODAL GREEN 3LW	3	5.5-6.0	S	25-35	45-60
SANODAL BLACK 2LW	10	4.2-4.7	**	55-60	30-40
SANODAL DEEP BLACK HBL LIQUID	10	5.5-6.0	S	55-60	30-40
SANODAL DEEP BLACK H3LW PASTE	10	5.5-6.0	S	55-60	30-40
SANODAL DEEP BLACK MLW	10	4.2-4.7	**	55-60	30-40

Buffer additions:

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

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

* For the first pH adjustment, oxalic acid or dilute ammonia solution or sodium hydroxide solution can be used, but afterwards only dilute sulphuric acid (approx. 20 %) or dilute ammonia solution or sodium hydroxide solution can be used to correct the pH. With Sanodal Gold 4N in no case must any other organic acids be used for this purpose.

** Here the pH is adjusted with either dilute acetic acid or formic acid, or else dilute sodium hydroxide solution.

AMOUNT OF DYE IN THE ANODIC COATING

The light and weather fastness of an anodic coating adsorptively dyed with organic dyestuffs depends on the following factors:

1. Depth of penetration of the dye
2. Amount of dye in the anodic coating
3. Sealing method used
4. Photochemical stability of the dyestuff molecule.

For light and weather fast dyed architectural elements conforming to the Sanodal standard, the following minimum amounts of dye in the anodic coating are required:

	AMOUNT OF DYE IN THE ANODIC COATING	
	[mg/dm ²]	[gm ²]
SANODYE YELLOW 3GL	12	1.2
SANODAL ORANGE 3LW LIQUID	22	2.2
SANODAL RED B3LW	20	2.0
SANODYE BLUE G	23	2.3
SANODYE BLUE 2LW	23	2.3
SANODAL TURQUOISE PLW LIQUID	35	3.5
SANODAL GREEN 3LW	23	2.3
SANODAL BLACK 2LW	25	2.5
SANODAL DEEP BLACK HBL LIQUID	40	4.0
SANODAL DEEP BLACK H3LW PASTE	45	4.5
SANODAL DEEP BLACK MLW	25	2.5

The amount of dye in the anodic coating is influenced both by the condition of the anodic coating and thus by the alloy and the anodization, and also by the dyeing conditions and the condition of the dye bath.

The amounts of dye in the anodic coating given above can readily be reached by following the prescribed Sanodal application directions. All these dyeings produce deeper shades. Medium and pale dyeings do not meet the light and weather fastness requirements.

If architectural alloys with unknown dye adsorption capacities are used, the amount of dye in the anodic coating should first be determined according to section 2.2, in order to be able to safeguard the minimum values.

COMPOSITION OF THE DYE BATH

The concentration of dye in the dye bath is an important factor influencing the amount of dye adsorbed in the anodic coating and thus the light and weather fastness of the dyeing. The dyeing conditions given in the table below must therefore be observed absolutely. The conditions have been selected so that the anodic coating is practically saturated with dyestuff. For this reason, increasing the concentration above the recommended amount when setting a fresh bath will bring no advantages. In used baths, reduced dyeing capacity due to contamination can be partially compensated by increasing the dye concentration (for maximum amounts see section 2.3). Better still, this is achieved by partial renewal of the baths, because in this way a portion of troublesome foreign ions are also removed.

The dyeing capacity is influenced not only by the dye content but also and above all by the content of foreign ions in the dye bath. Frequent control of the dyeing capacity is therefore extremely important (see section 2).

In particular, aluminum ions, phosphate ions and, depending on the dyestuff, also sulfate ions can impair the dyeing process considerably. It is therefore important to minimize the drag-in of foreign ions as far as possible.

INFLUENCE OF DYEING CONDITIONS

FACTORS	DEVIATION FROM PRESCRIBED METHOD	INFLUENCE OF THE DYEING PROCESS
DYEING TEMPERATURE	higher (> 60 °C)	Can lead to a pre-sealing process, and therefore tends to reduce the adsorption of dyestuff; lower light and weather fastness
DYEING TEMPERATURE	lower	Retards dye adsorption, prolongs the dyeing time. Usually better light and weather fastness
DYEING TIME	longer	Higher adsorption of dye; with overlong dyeing time, risk of dyestuff deposits on the surface
DYEING TIME	shorter	Lower adsorption of dye; lower light and weather fastness
PH OF DYE BATH	higher	Lower adsorption of dye (except for Sanodal Gold 4N); lower light and weather fastness
PH OF DYE BATH	lower	Anodic coating is attacked; higher concentration of aluminum in the dye bath

DYE MIXTURES ARE NOT PERMISSIBLE!

1.4 SEALING, AFTERTREATMENT

After dyeing and rinsing, the aluminum elements are sealed in either a one or a two-stage process. The exact working method is described in our technical information bulletins Anodal® ASL liquid and Anodal SH-1 liquid. In many cases Nickel sealing shows advantageous behavior. As dye deposited in the anodic coating can influence the sealing quality, it is necessary above all to observe the sealing time and the pH value in order to ensure the Sanodal quality of the dyeing results.

The sealing time is generally 2.5 min/μm at pH 5.6 ± 0.3. With Sanodye Blue G, Sanodye Blue 2LW, Sanodal Black 2LW and Sanodal Deep Black MLW the sealing time is 3 min/μm. Sanodal Gold 4N dyeings are sealed without nickel using Anodal SH-1 liquid.

INFLUENCE OF SEALING FACTORS

FACTORS	DEVIATION FROM PRESCRIBED WORKING METHOD	INFLUENCE
SEALING TIME	shortened	lower sealing quality; worse light and weather fastness
PH OF THE BATH	lower	impairment of the sealing; increased bleeding
TEMPERATURE	higher	increased smudge formation; (when using Nickel sealing) increased turbidity of the bath
	lower	lower sealing quality, increased bleeding

AFTERTREATMENT

After sealing, the pieces should be thoroughly rinsed with water and, if necessary, any remaining smudges must be removed. For cleaning, only neutral cleaning products and non scratching materials should be used.

For temporary protection during storage, transport and installation, the aluminum parts can be coated with a strippable lacquer or treated with a wax-containing material to improve their appearance.

1.5 COMBINATION DYEING

Electrolytic metal salt bronze colorations such as those produced with tin sulfate can be overdyed with Sanodal and suitable Sanodye dyes. In this way a wide variety of muted shades can be produced which meet the high fastness requirements of the Sanodal system.

Our technical information bulletin Anodal Color S-2 liquid provides further details concerning electrolytic coloration with tin salts.

Here it must be emphasized that also with these combination dyeings the prescribed working methods of the Sanodal system must be followed. In particular, the aluminum pieces must be thoroughly rinsed after the electrolytic bronze coloration to prevent metal salts from being dragged into the dye bath.

The electrolytic precolorations range from light to medium bronze. The member companies of Interoyd AG produce combination dyeings of this type under the name Sandalor^{®1} to a guaranteed quality standard.



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MONITORING THE WORKING PROCESSES

2.1 ANODIZATION

ANALYSIS OF THE ANODIZING BATH

Determination of the concentration of sulphuric acid and aluminum in the anodizing bath is carried out in the usual manner. We refer to the professional literature or the recommendations of Qualanod.

ELECTRIC CURRENT CONDITIONS

If any doubts exist concerning the instrument readings, the current density can be estimated as follows:

$$\text{Current Density} \left[\frac{\text{A}}{\text{dm}^2} \right] = \frac{\text{Anodic coating thickness} [\mu\text{m}]}{0.3 * \text{anodizing time} [\text{min}]}$$

ANODIC COATING THICKNESS

With every batch, the thickness of the anodic coating must be exactly measured by one of the following methods to $\pm 5\%$ precision:

- Eddy-current measuring method
- Light section microscope
- Traverse section measurement under a microscope
- Measurement of the breakdown voltage

RINSING AFTER ANODIZING

If deionized water is used in a second or third rinsing bath, the condition of the rinsing water can be controlled via its conductivity. A specific resistance of 10.000 Ohm*cm corresponding to a specific conductivity of 100 μS can be taken as guide value.

NEUTRALITY OF THE ANODIC COATING

Dry a small place on the anodic coating with blotting paper, place on it one drop of indicator solution (see section 2.6) and allow to dry for about 1 min (do not accelerate with blowing air). With an acid anodic coating the color will turn yellow, and with a neutral coating the color will turn a dull blue to blue-violet (entirely dry). This color effect is not lasting. Any indicator remaining on the coating does not affect further treatments.



2.2 DYEING CONTROLS

The dye baths and dyeing processes are monitored by controlling the following parameters:

- Temperature
- Dyeing time
- pH
- Dye content
- Relative dyeing power
- Amount of dye in the anodic coating

pH OF THE DYE BATH

The pH is measured with a glass electrode. The precision of the pH meter should be at least to ± 0.1 of a pH unit. pH papers are unsuitable for measuring the dye bath.

DYE CONTENT OF THE DYE BATH

The dye content of the dye bath is photometrically determined. A freshly prepared comparison dye solution is used as the standard. The dye bath is diluted to approximately the same color strength as that of the comparison solution.

DYESTUFF COMPARISON SOLUTIONS

	COMPARISON SOLUTION	1 ST DILUTION WITH DE-MINERALIZED WATER	2 ND DILUTION WITH BUFFER ADDITION	BUFFER ADDITION TO 2 ND DILUTION**	DILUTION FACTOR	CONCENTRATION OF COMPARISON SOLUTION	MEASUREMENT AT WAVELENGTH	EXTINCTION VALUE
	[g/l *C _n]	[ml] to 100 ml	[ml] 100 ml		[V _n]	[mg/l C _m]	[nm]	[E _n]
SANODYE YELLOW 3GL	3	10	5	A)	0.005	15	414	
SANODAL ORANGE 3LW LIQUID	3	20	20	A)	0.04	120	499	
SANODAL RED B3LW	5	10	5	A)	0.005	25	517	
SANODYE BLUE G	3	10	10	B)	0.01	30	631	
SANODYE BLUE 2LW	3	10	10	B)	0.01	30	637	Extinction values from the measuring
SANODAL TURQUOISE PLW LIQUID	5	10	5	B)	0.005	25	667	
SANODAL GREEN 3LW	3	20	20	A)	0.04	120	661	
SANODAL BLACK 2LW	10	10	5	A)	0.005	50	610	
SANODAL DEEP BLACK HBL LIQUID	10	10	10	A)	0.01	100	574	
SANODAL DEEP BLACK H3LW PASTE	10	10	10	A)	0.01	100	565	
SANODAL DEEP BLACK MLW	10	10	5	A)	0.005	50	612	

* corresponds to the initial concentration

** Buffer additions to the second dilution:

a) 1 ml buffer solution pH 5.6

b) 1 ml buffer solution + 20 ml dimethylformamide

Buffer solution pH 5.6:

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

Spectrophotometric measurements of the dye content exhibit sufficient precision when the measured values of the extinction (decrease in light strength) lie between 0.3 and 0.9. If the concentrations given in the previous table are selected to prepare the comparison solutions, the given dilutions will produce measuring solutions of suitable concentration (10 mm cuvette).

Since with certain dyes the extinction values and measurement wavelengths are clearly influenced by the solvent and the pH value, the buffer addition given above must be added with the second dilution.

CALCULATION OF THE DYE CONTENT

The dye content of the bath is calculated as follows:

$$C = E * C_n * \frac{V_n}{E_n * V}$$

C Dye content of dye bath g/l

C_n Content of comparison solution g/l

E Extinction value of dye bath

E_n Extinction value of comparison solution

V Dilution factor of dye bath

V_n Dilution factor of comparison solution

Provided the dye bath has been diluted for the measurement by the same factor as the comparison solution, the dyestuff content can be calculated in a more simple manner as follows:

$$C = E * \frac{C_n}{E_n}$$

This method applies to all the Sanodal and Sanodye dyes with the exception of Sanodal Gold 4N. The content of Sanodal Gold 4N is determined titrimetrically. This method is described in detail in our technical information bulletins for these dyes.

RELATIVE DYEING POWER OF THE DYE BATH

In order to evaluate the dyeing power of a used bath, a comparison dyeing is made: The dye bath is replenished to the required concentration and then an oxidized aluminum plate is dyed in it. Meanwhile another plate is dyed with a freshly prepared standard solution having the same concentration.

A spectrophotometric measurement of the amount of dye in the anodic coating by measuring the reflection of a dyed sample does not permit a sufficiently precise comparison. For this reason the dye amount is determined by stripping the two unsealed test dyeings with a tartrate containing sodium hydroxide solution and then measuring the extinction value of the stripped solutions.

This procedure requires two aluminum test plates for a double measurement. As only comparison values are needed, it is unnecessary to use the alloy employed for production. Plates of approx. 0.5 mm thickness made of pure aluminum or AlMgI for example, are quite suitable. Cut the edges off an anodized plate and discard. Now cut out two adjacent pieces measuring 100x50 mm.

Dye the two pieces under exactly the same conditions, one in the bath sample and the other in the standard solution, as described in section 1.3. Afterwards rinse the specimens for a short time and then pat dry with a filter paper and hang in the air to dry out completely.

Cut off a 10 mm strip around the edge of each specimen and discard. Then from each dyed specimen cut two strips of 10x80 mm, which will now be used for the double measurement of the dye content. Place each test specimen in an extraction tube (\varnothing 13 mm, length 165 mm) into which is then placed 12 ml stripping solution (12 g/l NaOH + 7.5 g/l L[+] tartaric acid), seal with a rubber stopper and shake until most of the dyestuff has been stripped (30–120 sec). Then pour the solution into a 100 ml or 200 ml measuring flask containing 0.6 ml acetic acid 100%. After a short rinse with deionized water, repeat the procedure in order to strip off any remaining dyestuff and then rinse into the measuring flask. Here the development of hydrogen owing to bare aluminum should be avoided as much as possible, so as to prevent the reduction of the dyestuff. Fill up each solution with deionized water to 100 ml or 200 ml respectively, and measure spectrophotometrically (see following table).

DYE	MEASURING VOLUME	WAVELENGTH
	[ml V _A]	[nm]
SANODYE YELLOW 3GL	200	414
SANODAL ORANGE 3LW LIQUID	100	499
SANODAL RED B3LW	100	517
SANODYE BLUE G	100*	631
SANODYE BLUE 2LW	100*	637
SANODAL TURQUOISE PLW LIQUID	200**	667
SANODAL GREEN 3LW	100	661
SANODAL BLACK 2LW	100	610
SANODAL DEEP BLACK HBL LIQUID	100	574
SANODAL DEEP BLACK H3LW PASTE	100	565
SANODAL DEEP BLACK MLW	100	612

* An additional 20 ml dimethylformamide must be added to the measuring flask

** An additional 40 ml dimethylformamide must be added to the measuring flask

CALCULATION OF THE RELATIVE DYEING POWER

If all the test surfaces are exactly the same size, the relative dyeing power is calculated as follows:

$$D = 100 * \frac{E}{E_n} \geq 85\%$$

If the surfaces are not of the same size, they must be separately measured to 0.1mm precision and the calculation is made as follows:

$$D = 100 * E * \frac{F_n}{E_n * F} \geq 85\%$$

- D Relative dyeing power in %
- E Extinction value of the stripped dye bath dyeing
- E_n Extinction value of the stripped comparison solution dyeing
- F Area of the dyed metal strip from the dye bath
- F_n Area of the dyed metal strip from the comparison solution

AMOUNT OF DYE IN THE ANODIC COATING

The quality requirements in the Sanodal system can only be safeguarded if the dye amounts given in section 1.3 »Amount of dye in the anodic coating« are reached. In the same way as the measurement of the relative dyeing power, for this control the test dyeings are stripped and the dyestuff amounts are measured spectrophotometrically.

Here the dye comparison solutions are taken as the standard (see section 2.2 under »Dye content of the dye bath«).

CALCULATION OF DYE AMOUNT IN THE ANODIC COATING

The area concentration in mg/dm² is calculated as follows:

$$C_t = \frac{E * C_m * V_a}{E_n * 10 * F}$$

- C_t Area concentration in mg/dm²
- C_m Concentration of the comparison measuring solution
- E Extinction value of the stripped test dyeing
- E_n Extinction value of the comparison measuring solution
- F Precisely measured area of the test plate in cm² (take both sides into account!)
- V_a Measuring volume of the stripped test dyeing in ml

2.3 DYEING CORRECTIONS

pH OF THE DYE BATH

Optimum dyeing results are only achieved when the pH values of the dye baths are constantly monitored and corrected as necessary.

DYE	REQUIRED pH RT	ADJUSTED ↓ WITH:	ADJUSTED ↑ WITH:
SANODYE YELLOW 3GL	5.5-6.0	acetic acid	sodium hydroxide
SANODAL GOLD 4N	4.0-4.7	sulphuric acid	sodium hydroxide
SANODAL ORANGE 3LW LIQUID	5.5-6.0	acetic acid	sodium hydroxide
SANODAL RED B3LW	5.5-6.0	acetic acid	sodium hydroxide
SANODYE BLUE G	5.5-6.0	acetic acid	ammonia
SANODYE BLUE 2LW	5.5-6.0	acetic acid	ammonia
SANODAL TURQUOISE PLW LIQUID	5.5-6.0	acetic acid	sodium hydroxide
SANODAL GREEN 3LW	5.5-6.0	acetic acid	sodium hydroxide
SANODAL BLACK 2LW	4.2-4.7	acetic or formic acid	sodium hydroxide
SANODAL DEEP BLACK HBL LIQUID	5.5-6.0	acetic acid	sodium hydroxide
SANODAL DEEP BLACK H3LW PASTE	5.5-6.0	acetic acid	sodium hydroxide
SANODAL DEEP BLACK MLW	4.2-4.7	acetic or formic acid	sodium hydroxide

Acetic or formic acid approx. 40 %

Sulphuric acid approx. 20 %

Sodium hydroxide and ammonia approx. 10 %



DYE CONTENT OF THE DYE BATH

A correction of the dye consumed has to be made at the very latest before the actual concentration drops below 85% of the required concentration.

The calculated amount of dye is pre-dissolved with the required volume of water. In this way it can also be controlled whether the dye is dissolved. The replenishment is calculated as follows:

$$\text{Replenishing dye [g]} = (C_n * V_n) - (C * V)$$

$$\text{Replenishing water [l]} = V_n - V$$

C_n Required value for dyestuff [g/l]

C Actual value for dyestuff [g/l]

V_n Required value for bath volume [l]

V Actual value for bath volume [l]

RELATIVE DYEING POWER

An increased concentration of foreign ions will diminish the dyeing power of the dye bath, despite a correct dyestuff concentration. Corrective measures can be taken at any time, but must be taken if the dyeing power at the required concentration becomes less than 85% of a freshly prepared solution. Independently of this, the minimum amounts of dyestuff in the anodic coating given in section 1.3 must be reached at all times.

The correction of reduced dyeing power of the dye bath can be carried out by increasing the required concentration, by partial renewal of the dye bath, or by a combination of both measures. Correction by increasing the required dyestuff concentration is only of limited applicability, as the maximum dyestuff amounts given in the following table can not be exceeded.

DYE	REQUIRED CONTENT	MAXIMUM CONTENT
	[g/l]	[g/l]
SANODYE YELLOW 3GL	3	5
SANODAL GOLD 4N	10-30	40
SANODAL ORANGE 3LW LIQUID	3	5
SANODAL RED B3LW	5	7
SANODYE BLUE G	3	4
SANODYE BLUE 2LW	3	4
SANODAL TURQUOISE PLW LIQUID	5	8
SANODAL GREEN 3LW	3	4
SANODAL BLACK 2LW	10	15
SANODAL DEEP BLACK HBL LIQUID	10	15
SANODAL DEEP BLACK H3LW PASTE	10	15
SANODAL DEEP BLACK MLW	10	15



If, after increasing the dye content to the maximum concentration, the relative dyeing power is still less than 85 %, the bath must be at least partially renewed.

More effective than increasing the dye content, the dyeing power of the dye bath can be improved by partial renewal. The advantages of this method are:

- More homogeneous dye bath condition
- Constant partial removal of troublesome foreign substances
- The need for setting a new bath can be considerably postponed

The effectiveness of a partial dye bath renewal is tested in the laboratory as follows: An arbitrary portion (e.g. 20–50 %) of a dye bath sample, adjusted to the required concentration of dye but with a dyeing power of less than 85 % is replaced with fresh dye solution in the initial concentration. Then the dyeing power of this partially renewed bath is determined.

If the dyeing power is now more than 85 %, the same procedure is applied to the complete dye bath.

The content of foreign ions in the dye bath can be kept under control by periodical partial renewals so that the dyeing power never falls below 85 %. Naturally, because these troublesome foreign substances are always only partially removed, the dyeing power is always less than the required value of 100 %. By combining a partial renewal with an increase of the dyestuff content over the required concentration (up to the limit given in the table), in many cases a dyeing power of 100 % compared with the required concentration can be attained.

Every substantial partial renewal or even a complete renewal has a distinct effect on the dyeing properties. It is therefore advisable to make the partial dye bath renewal as frequent but as moderate as possible, corresponding to the amount of drag-in. As the dragged-in amount of contamination is usually greater than that which is eliminated, it is recommended to replace a portion of the dye bath regularly, regardless of analytical results.

2.4 SEALING

Constant control and correction of the sealing baths is absolutely necessary in order to achieve and maintain the required sealing quality.

The baths are monitored by controlling the following parameters:

- Temperature
- pH
- Concentration
- Sealing quality



pH OF THE SEALING BATHS

The pH is measured with a glass electrode. The pH meter should be precise to at least ± 0.1 of a pH unit. pH papers are unsuitable for measuring the sealing bath.

CONTENT OF THE SEALING BATHS

The methods used for determining the content of Anodal ASL liquid and Anodal SH-1 liquid are described in detail in our technical information bulletins for these products.

SEALING QUALITY

Owing to drag-in, the content of foreign ions in the sealing bath can reach high amounts. This leads to turbidity of the bath, increased smudging and reduced sealing quality. For this reason, even with a correct working method, the sealing quality must be regularly tested according to ISO 3210 (weight loss in chromic phosphoric acid).

Under the terms of the Sanodal system the weight loss according to ISO 3210 of 20 mg/dm² must not be exceeded.

Correctly sealed dyeings which follow to our prescribed working methods generally meet this standard (see also section 3.4).

2.5 MONITORING SCHEDULE

The processes in the prescribed working methods we have described must be checked regularly, so that they correctly fulfill their purpose. We recommend following intervals depending on the usage of the baths:

PROCESS	CONTROL	FREQUENCY
ANODIZING	Temperature	constantly
	Current density	constantly
	Voltage	constantly
	Time	constantly
	Sulphuric acid content	weekly
	Aluminum	weekly
	Anodic coating thickness	every bath load
RINSING BATH	Water conductivity	constantly
	Neutrality of anodic coating	spot checks
DYEING	pH	daily
	Temperature	constantly
	Time	constantly
	Dyestuff content	
	- in use	daily
	- after standing	before starting dyeing
	Dyeing power	
	- in use	weekly
	- after standing	before starting dyeing
	- in case of trouble	immediately
Amount of dye in anodic coating	with changes in the prescribed Sanodal working methods, alloys, anodizing and dyeing	
SEALING	pH	constantly
	Temperature	constantly
	Time	constantly
	Content	weekly
	Sealing quality	every bath load

2.6 EQUIPMENT OF CONTROL LAB

In order to be able to carry out the required operating controls, a laboratory with the usual basic equipment is required. In addition, the following instruments are needed:

- Spectrophotometer
- Anodic coating thickness measuring device
- Apparent conductivity measuring device

CHEMICALS	REAGENTS	FURTHER DETAILS
RINSING, NEUTRALITY, ANODIC FILM	pH indicator	1g bromocresol purple dissolved in 1l ethanol
DYE BATH CONTENT	Buffer additions	Ammonium acetate Dimethylformamide Acetic acid 100 %
SANODAL GOLD 4N CONTENT	Indicator	5-sulphosalicylic acid-dihydrate
	Potassium permanganate 0.2N	KMnO ₄ 0.1N
	EDTA solution 0.1M	
	Buffer	Sodium acetate anhydrous Chloroacetic acid
DYE BATH DYEING POWER	Acetic acid	Acetic acid 100 %
	Stripping solution	L(+) tartaric acid Sodium hydroxide 100 %
ANODAL SH-1 LIQUID CONTENT	Measuring reagent colorimetric and spectrophotometric	Ammonium hydrogen difluoride Iron (III) chloride hexahydrate L(+) tartaric acid
ANODAL ASL LIQUID CONTENT	EDTA solution 0.1M	
	Indicator	Murexid Sodium chloride
	Ammonia	Ammonia solution 25 %

3

PROPERTIES OF THE FINISHED ALUMINUM

The physical and chemical properties of anodic coatings dyed according to the working methods prescribed here are practically identical with those of corresponding undyed anodic coatings.

3.1 NATURAL WEATHERING

In a wide-scope weathering fastness study, dyed aluminum specimens were exposed in widely diverse climatic conditions both in the northern and southern hemispheres. The dyed specimens were exposed at a 45° angle to the earth's surface, facing south in the northern hemisphere and north in the southern hemisphere. The exposure conditions were thus more severe than on a vertical building facade. The test specimens were only cleaned and the smudge removed after the exposure time was over.

The results of these 10-year weathering tests showed that the fastness properties of the specimens dyed according to the Sanodal process were equivalent and in many cases actually superior to inorganic iron oxalate gold colorations which, as is well known, have been used for decades in the architectural and construction industry and whose weather fastness is recognized as being adequate.

The behavior of undyed and dyed aluminum with respect to climatic influences is approximately the same. While in sea climates, strong solar radiation and high precipitation exhibit no markedly harmful influence, industrial air contaminations, depending on their aggressivity, lead to a corrosive removal of the anodic coating with corresponding loss of color.



3.2 ARTIFICIAL LIGHT AND WEATHERING EXPOSURE

Artificial light and weathering exposure tests provide mutually comparable and reproducible results, but are not always equivalent to natural weathering. As a result, the evaluation of artificial light and weathering exposure is only applicable to natural conditions with reservations.

LIGHT FASTNESS OF SANODAL SYSTEM

Evaluation of the light fastness was made according to ISO 2135. All dyestuffs of the Sanodal system exhibit a light fastness rating of >9.

FASTNESS PROPERTIES OF SANODAL COMBINATION DYEINGS

Light and weathering fastness tests as well as sealing quality tests have shown that Sanodal combination dyeings exhibit at least the same fastness properties as the corresponding pure Sanodal system dyeings.

3.3 ARTIFICIAL CORROSION

KESTERNICH TEST

According to DIN 50018:

Humidity-alternating climate with sulfur dioxide-containing atmosphere:

2l SO₂ addition per cycle.

1 cycle = 24 h

(8 h preheating 40 °C ± 3 °C, 16 h cooling at room temperature).

SALT-SPRAY TEST CASS

According to ISO 3770 (CASS-DIN 50021):

50 g/l NaCl + 0.26 g/l CuCl₂ · 2H₂O

adjusted with acetic acid to pH 3.1–3.3,

25 °C ± 2 °C, testing temperature 50 °C ± 1 °C,

testing time 48 h.

The dyeings presented show no differences on the surface of the test plates from the undyed specimens.

SALT-SPRAY TEST NSS

According to ISO 3768 (NSS-DIN 50021):

50 g/l NaCl, pH 7, testing temperature 35 °C,

testing time 1000 h.

DYE	EVALUATION AFTER 6 CYCLES
UNDYED	1-2
SANODYE YELLOW 3GL	1-2
SANODAL GOLD 4N	2
SANODAL ORANGE 3LW LIQUID	1-2
SANODAL RED B3LW	1-2
SANODYE BLUE G	2
SANODYE BLUE 2LW	2
SANODAL TURQUOISE PLW LIQUID	1-2
SANODAL GREEN 3LW	1-2
SANODAL BLACK 2LW	2
SANODAL DEEP BLACK HBL LIQUID	1-2
SANODAL DEEP BLACK H3LW PASTE	1-2
SANODAL DEEP BLACK MLW	2

0 unchanged

1 very slight attack (surface slightly cloudy)

2 slight attack (surface cloudy to lightly spotted)

3 medium attack (bleaching-out, decoloration, spots, loss of gloss)

4 heavy attack (incipient peeling of film, heavy decoloration, pitting)

5 total attack (film mostly peeled off, total decoloration, pitting)

DYE	CORROSION
UNDYED	none
SANODYE YELLOW 3GL	none
SANODAL GOLD 4N	slight
SANODAL ORANGE 3LW LIQUID	very slight
SANODAL RED B3LW	slight
SANODYE BLUE G	slight
SANODYE BLUE 2LW	very slight
SANODAL TURQUOISE PLW LIQUID	very slight
SANODAL GREEN 3LW	slight
SANODAL BLACK 2LW	none
SANODAL DEEP BLACK HBL LIQUID	none
SANODAL DEEP BLACK H3LW PASTE	none
SANODAL DEEP BLACK MLW	none

3.4 SEALING QUALITY

WEIGHT LOSS TEST

Experience has shown that the weight loss test gives very good results for evaluating the quality of an anodic coating.

As a rule, the weight loss values for Sanodal process dyeings obtained in the immersion test with phosphoric-chromic acid solution according to ISO 3210 are less than 30 mg/dm². However, despite the same sealing, the weight loss value may vary, depending on the alloy and the anodization. For this reason, specific standards must be defined for each individual material. If the weight loss of the test specimen is higher than the standard value valid for the material in question, then a sealing defect exists.

ADMITTANCE TEST

The admittance (apparent conductivity) value, measured and calculated as the Y20 value according to ISO 2931, is above all a criterion for the quality of the sealing. Despite the same sealing, this value may vary, depending on the alloy, the anodization and above all the dyeing process used. For this reason, specific standards must be defined for each individual material. If the admittance value is higher than the standard value valid for the material in question, a sealing defect exists.

The limit value given in the Qualanod Guidelines of $Y_{20} = 20 \mu\text{S}$ applies only to colorless anodized alloys of the type defined in the guideline.

Inferences from the admittance value as to the behavior of the material under a given stress are only permissible when a well-founded correlation exists between the two magnitudes.

DYE SPOT TEST

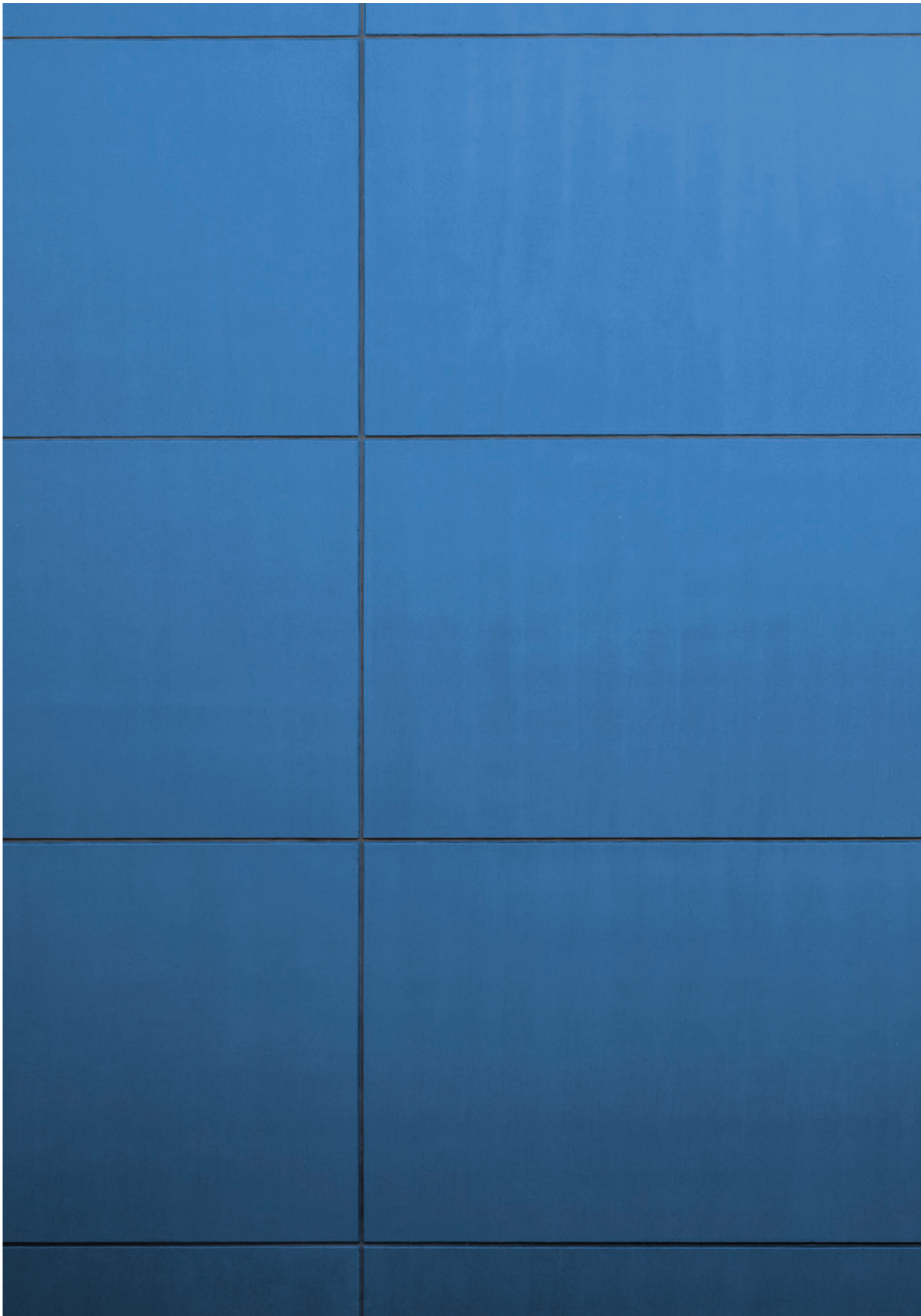
A further method for assessment of the sealing quality is the »Dye Spot Test« according to ISO 2143. For this assessment, the still remaining greater or lesser porosity of the sealed anodic film is utilized by observing whether certain suitable dyes have an influence on the coating.

The surface to be tested is first cleaned from grease and soil with acetone. Then a drop of hexafluorosilicic acid (25 ml/l, $d = 1.29 \text{ g/ml}$) is applied and allowed to stand for 1 minute (23 °C), after which the surface is rinsed and dried. A solution of 5 g/l Sanodye Blue 2LW is prepared and the pH adjusted to 5.0 ± 0.5 with dilute sulphuric acid or dilute sodium hydroxide solution. One drop of this solution is applied to the spot previously treated with acid and allowed to stand for 1 minute (23 °C). Afterwards the spot is rinsed with water and then treated by mechanical rubbing with magnesia, for example. Afterwards the spot is rinsed and dried. Very little or no visible coloration indicates that the quality of sealing is good. An exact assessment is made with a comparison scale according to ISO 2143.

3.5 ABBREVIATIONS

ABBREVIATIONS

DIN	Deutsches Institut für Normung (German Institute for Standardization)
ISO	International Organization for Standardization
EMPA	Eidgenössische Materialprüfungsanstalt (Swiss Federal Laboratories for Materials Science and Technology), CH-8600 Dübendorf
ASTM	American Society for Testing and Materials
Qualanod	Association for Quality Control in the Anodizing Industry





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