Sanodal® Gold 4N

For gold shades of high fastness on anodised aluminium

Sanodal Gold 4N is a water-soluble product based on ferrioxalate for the chemical dyeing of artifically produced oxide films on aluminium in gold shades of high fastness.

This technical information bulletin contains the following information on the features and application of **Sanodal Gold 4N**:

- Properties
- Optimum application and working method
- Maintenance of dyebaths
- Analytical methods of bath monitoring
- Influence of processing parameters and dyeing conditions
- Factors impairing bath stability.

1. Brief characterization

Sanodal Gold 4N is a ferrioxalate-based preparation in powder form. This **Sanodal** product is for attaining gold shades of high fastness on artificially produced aluminium oxide films. Compared to conventional ammonium ferrioxalate, **Sanodal Gold 4N** is distinguished by higher photochemical stability in solutions.

2. Properties

Commercial form	greenish yellow powder
Storage stability	practically unlimited. Protect product from effects of light and moisture. Any lumps that may form have no influence on the product's dyeing properties.
Solubility	at 25°C: 430 g/l water at 65°C: 750 g/l water
Bulk density	550 g/l
pH of product	4.0 ± 0.5 at 30 g/l
Ecotoxicological data	see Safety Data Sheet.

3. Scope of application and colour scale

Aqueous **Sanodal Gold 4N** solutions can be used to produce gold shades of high fastness to light, weather, corrosion and heat on chemically or - preferably - anodically produced oxide films on aluminium and its alloys. The dyeings are produced by the hydrolytic incorporation of inorganic hydrated iron oxide colour pigments in the oxide film.

The colour scale depends on the working method and ranges from new silver to pale brass to gold tones of extremely varied degrees, even to brownish orange. The colour scale can be extended even to attractive browns by overdyeing aluminium sections that have been electrolytically precoloured in bronze tones.

Sanodal Gold 4N solutions can also be used to decolourize difficult-to-remove adsorption-dyed shades.

Thanks to their high resistance, **Sanodal Gold 4N**-dyed aluminium sections can be used in a wide variety of industrial applications, e.g. the finishing of audiovisual equipment, jewellery, signs and nameplates, household articles and, in the framework of the **Sanodal System**, also for facade elements in the construction industry.

4. Application

- Substrate
  Chemically or - preferably - anodically produced unsealed oxide films on aluminium or its alloys (whether uncoloured or electrolytically precoloured).
- Application technique
  Immersion in aqueous solutions with bath agitation, or by spraying.
- Water quality
  It is recommended to use deionized water.
- Application amounts

Shades	**Sanodal Gold 4N**
pale medium to deep	10 - 20 g/l 20 - 30 g/l

- Dyeing temperature
  40-55°C, for pale shades also 30-40°C
- pH of baths
  between 4.0 and 5.0
- Dyeing time
  0.5 - 20 min, depending on desired shade, but preferably for 2-10 min
- Sealing
  The dyed oxide films must afterwards be sealed according to the guidelines for anodized aluminium. It is recommended to seal in boiled water with 2 ml/l **Anodal® SH-1 Liquid**.

5. Dye solutions - setting, application, maintenance

5.1 Dyebath and feed tanks

The ideal material for the dyeing tanks and feed equipment is acid-resistant high-grade steel based on Cr, Ni or Mo. Tanks made of normal steel and aluminium with acid-resistant, inorganic or organic-based linings (enamel, rubber, polyester, polyvinyl chloride, etc.) are also suitable. However, it should be borne in mind that even tiny leakages can result in an impairment of the dyeing process.

5.2 Setting and reinforcing dyebaths

Before being added to the bath, **Sanodal Gold 4N** must be dissolved in at least three times the amount of water, which should be as hot as possible.

5.3 Water quality

Deionized or very soft water should be used. If no such water is available, it is essential to add 2-5 g/l oxalic acid.

5.4 Bath circulation

For high uniformity of dyeings, the dyebath must be kept in moderate agitation shortly before and during the dyeing process, e.g. by blowing in air through pipes or with a circulation pump.

5.5 Standing time and service life of dyebaths, consumption of product

With careful adherence to our recommendations, dye solutions can be used almost indefinitely. In our experience, the service life of dyebaths, with normal throughput and minimal maintenance expenditure, lasts from 6 months to 2 years.
Depending on the depth of shade, the consumption of the product for pigmentation is between 0.1 and 10 g/m^2 **Sanodal Gold 4N**.
The drag-out loss ranges from 1.5-5 g/m^2. Depending on the shade depth, the guide value for overall consumption, including bath renewal is 20-30 g/m^2 **Sanodal Gold 4N.**

5.6 Storage of dye solutions

When not in use, the **Sanodal Gold 4N** solution should be immediately protected as far as possible from light and air by covering the dyeing tank or storage in a closed tank.

5.7 Disposal

Disposal of spent dyebaths must be carried out in accordance with local wastewater regulations according to the recommendations given in our technical information bulletin entitled "**Anodal WT-1 Liquid**".

5.8 Control and reinforcing of the dyebath

For dyebath maintenance, in addition to constant monitoring of the dyeing properties, the control operations and correctional measures described below must be used. It is recommended to carry these out periodically using experiential values, especially when problems occur and after prolonged non-use of the bath.

- **Sanodal Gold 4N** concentration
  This measurement is carried out as described in Section 6.1. If the concentration is found to be inadequate, add the calculated amount of **Sanodal Gold 4N** in concentrated form.

- Relative oxalate concentration
  This is also determined as described in Section 6.1. The actual oxalate content must correspond at least to the concentration calculated on the composition of **Sanodal Gold 4N** (= 100%). This has been found to range from 110 to 140%. If the measured value is less than 110%, add 2-5 g/l oxalic acid.

- pH
  The pH of the dyeing solution can be measured with the aid of a pH meter. For a quick measurement, pH indicator paper can also be used.
  In case of deviation from the recommended pH range between 4.0 and 5.0, the pH is corrected with dilute sulphuric acid, or else with dilute caustic soda solution or ammonia.

- Appearance of separated decomposition products
  Sanodal Gold 4N forms clear, greenish yellow solutions; these charracterize an excellent condition of the bath. When the greenish tinge disappears, the colour shifts to brown or cloudiness occurs and decomposition as described in Section 8 is present.

6. Analytical monitoring of Sanodal Gold 4N baths

6.1 Titrimetric analysis

Reagents

- 0.2 N-$KMnO_4$ (potassium permanganate)

  In a measuring flask, dilute a normal concentrate (e.g. Titrisol+ Merck No. 9935) adjusted for the preparation of 1 litre of a 0.1 N solution, to 500 ml.
  Concentration: 6.32 g potassisum permanganate in 1000 ml solution.

- M-EDTA (ethylene diamine tetraacetic acid)

  In a measuring flask, dilute a normal concentrate (Titriplex+ III Merck No. 9992) adjusted for the preparation of 1 litre of a 0.1 N solution, to 1000 ml.
  Concentration: 37.2 g ethylene diamine tetraacetic acid, disodium salt, MW 372, in 1000 ml solution.

- Buffer/Indicator solution
  164 g sodium acetate anhydrous p.a. (MW 82)
  100 g chloracetic acid cryst. pure (MW 94.5) and
  10 g 5-sulphosalicylic acid pure (MW 254.2) as indicator
  have to bedissolved in deionized water, and diluted to 1000 ml in a measuring flask .

- Sulphuric acid 20%.

Analysis procedure

Take a sample from the production dyebath and clarify by filtration, e.g. through a folded paper filter, discarding any cloudy first runnings. Using a transfer pipette, take 20 ml of the clear filtrate and, while heating and stirring, add this to 100 ml deionized water and 10 ml sulphuric acid 20%. When this solution reaches 50-60°C add dropwise from a burette 0.2 N-$KMnO_4$ until the yellowish solution takes on a steady pale pink coloration.

Consumption: a ml 0.2 N-$KMnO_4$ (ca. 25 ml with 30 g/l **Sanodal Gold 4N**)

At the same temperatuare, now add 20 ml buffer/indicator solution. Add dropwise from another burette 0.1 M-EDTA to this cloudy red mixture until the red colour disappears.

Consumption: b ml 0.1 M-EDTA (ca. 8 ml with 30 g/l **Sanodal Gold 4N**).

Calculation

Concentration of **Sanodal Gold 4N** in g/l:

$$C_{4N} = 3.6 \cdot b$$

Relative concentration of the oxalate in % :

The relative concentrations indicates the molar oxalate/iron ratio, where the ratio 3 moles of oxalate (264 g) to 1 mole of iron (55.9 g) is defined as 100%.

$$C_{Ox} = 33.3 \frac{a}{b}$$

		C_{Ox}
pure **Sanodal Gold 4N**	=	100%
with excess oxalate	>	100%
with insufficient oxalate	<	100%
minimum value	=	110%
maximum value	=	140%

6.2 Proof of ferrooxalate

Reagents

- Potassium ferricyanide 5%
  Disssolve 5 g potassium ferricyanide (red prussiate of potash) in 100 ml deionized water. Store this reagent in the dark.
- Sulphuric acid 20%

Identification reaction

To approx. 2 ml of the unfiltered dyeing solution, add 2 drops of sulphuric acid 20% and 2 drops potassium ferricyanide 5% and boil up for a short time. A blue-green colour indicates the presence of ferrooxalate, which is produced by the decomposition of **Sanodal Gold 4N** under the effect of light or metal. The blue coloration must appear immediately.

6.3 Proof of hydrogen peroxide

Reagents

- Potassium iodate starch paper

Identification reaction

On the reagent paper, place a drop of the acid dyeing solution to which H_2O_2 has been added for the purpose of regeneration. A violet coloration indicates the presence of H_2O_2.
Note: Make further additions of H_2O_2 only in the case of a positive ferrooxalate and a negative H_2O_2 reaction.

7. <u>Notes on dyeing</u>

The final shade depth depends on the properties of the anodic film (thickness and porosity) and the dyeing conditions. The parameteres are defined on the basis of laboratory trials or experiential values so that the film can achieve the required protective effect and the desired shade can be produced within the defined processing time. For high reproducibility, the parameters, once defined, must be adhered to as exactly as possible by monitoring the oxidation and dyeing process. Any deviations must be offset by adjusting the dyeing time (sampling by comparison with a standard dyeing sample).

7.1 Substrate

The shade depth increases along with increasing thickness and porosity of the anodic film. These two influential factors depend in turn on the alloy, anodizing time, temperature, current density and composition of the acid electrolyte.

7.2 Sanodal Gold 4N concentration

The exact concentration of **Sanodal Gold 4N** in the bath is not to be regarded as a critical factor, and normal fluctuations have practically no effect with short dyeing times (pale gold shades). It is recommended, however, especially in cases where the dyeing power deviates distinctly from the normal, to monitor the concentration of the dye in the bath.

7.3 pH

Owing to the drag-in of anodizing acid as well as film detachment and the effect of air and light, the pH value can change, despite its inherent buffering. As a rule, under production conditions a gradual rise in the pH is observed.
At pH values below 4 the dyeing power diminishes rapidly, and at pH values over 6, hydrolysis takes place with the precipitation of ferrihydroxide.

7.4 Dyeing temperature

With rising temperature of the dyebath the rate of dyeing greatly increases. In order to achieve acceptable dyeing times, it is preferable to use the lower temperature range (30-40°C) for pale shades and the upper range (40-55°C) for deeper tones. Above 60°C the maximum attainable shade depth becomes progressively lower as a sealing effect sets in.
Low dyeing temperatures can later facilitate any stripping of the dyeing which may become necessary.

7.5 Dyeing time

By adjusting the dyeing time, a wide range of colours can be covered. The other operating parameters such as film structure, dyeing temperature and dyestuff concentration should be selected so that the desired shade is produced in a time span ranging from 30 s to 30 min, preferably within 2-5 min.
For reasons of shade uniformity, especially with large-surfaced aluminium parts, dyeing times of less than 30 s should be avoided.
Once the dyeing time is set, it should not be deviated from by more than 10 s for pale dyeings and 1 min with deep shades.

7.6 Additions for stabilization of the solution

Sanodal Gold 4N exhibits extremely high solution stability in the presence of oxygen and excess oxalate. For this reason it is recommended to add 2-5 g/l oxalic acid and to circulate air through the bath while it is in use.
The oxalate is used up due to the action of air and light. On the other hand, the dyeing power decreases with increasing oxalate concentration. For this reason it is essential to keep the oxalate concentration within the defined limits by periodically checking the relative oxalate concentration according to Section 6.1 and to supplement it as necessary.

8. <u>Notes on bath maintenance</u>

Apart from the consumption related to processing, **Sanodal Gold 4N** solutions exhibit only limited stability. This applies even more strongly to the usual commercial ammonium ferrioxalates. Observance of the following recommendations as well as those in Section 5 will ensure virtually unlimited service life of the dyeing solutions.

8.1 Alkalis

If the pH exceeds the upper limit value, hydrolysis takes place and a gel-like, brown ferrioxide hydrate precipitates. This can be corrected, as described in Section 5.8.

8.2 Effect of air

The effect of atmospheric oxygen results in oxidative degradation of the oxalate. On the other hand, oxygen counteracts the decomposition due to light described below in Section 8.3 by keeping the iron at the higher, "ferri" stage, which is effective for dyeing. For this reason it is recommended to introduce air into the bath during its exposure to light, i.e. while it is in use, or even to add hydrogen peroxide. However, this entails the periodical replacement of the degraded oxalate, as described in Section 5.8. Otherwise brown ferrioxide hydrate will precipitate, despite maintenance of a constant pH. Degradation of the oxalate involves a rise in the pH.

8.3 Effect of light

Due to the effect of light, the dissolved **Sanodal Gold 4N** undergoes a photochemical, intramolecular reaction and decomposes into ferrooxalate, which is ineffective for dyeing purposes. This slowly precipitates as a fine crystalline, yellowish suspension. Oxygen and oxalate counteract this reaction. Any ferrooxalate which has formed can be converted back into **Sanodal Gold 4N** by adding hydrogen peroxide and oxalate (see Section 5.8).

8.4 Water hardness

Water hardness extracts the oxalate from **Sanodal Gold 4N** and precipitates it in the form of a white suspension of earth alkali oxalates. The results correspond to the oxidative degradation of the oxalate described in Section 8.2.

8.5 Contact with base metals

On contact with base metals such as normal steel or non-anodized aluminium, ferrooxalate is formed. Its appearance and correction are described in Section 8.3 above.

8.6 Bath contamination

The state of the solution and the dyeing power are not greatly affected by the drag-in of anodizing acid (sulphates, aluminium). For this reason, no special requirements are demanded for the rinsing operation. However, the entrainment of other chemicals must be avoided, especially phosphates and hardness elements from degreasing, lustre or etching baths.

9 Summary of measures to be taken

All the reactions mentioned in Sections 8.1 to 8.5 cause a reduction in the concentration of **Sanodal Gold 4N.** This reduction is not critical and can be corrected by replenishing it, in the same manner as the consumption of the dye for processing. Precipitations visible to the eye do not affect the dyeing process and are not a disturbing factor. More serious, however, is the fact that sparingly soluble decomposition products in a colloidal transition stage can impair the uptake of **Sanodal Gold 4N** - even when its solution is intact - by closing the pores of the film. As a result, due attention must be given to proper maintenance of the dyebath. If the dyebath continues to be used despite cloudiness, the restoration of the bath is made more difficult owing to the ageing of the precipitates.

Survey

Alteraton	Causes	Corrective measures
Brown coloration, precipitation of gel -like ferrioxide hydrate	pH too high Lack of oxalate due to - effect of air - water hardness	Correct the pH Add oxalate, use deionized water, protect from effect of air when not in use.
Formation of ferrooxalate, yellowish precipitate	Effect of light, contact with base metals	Protect dyeing solution from effect of light and air. Add hydrogen peroxide, add oxalate.
Separation of white calcium oxalate	Water hardness	Use deionized water, add oxalate

The following recommendations can therefore be made for correct bath management:

- **Sanodal Gold 4N concentration**
  Determine as described in Section 6.1 and
  Replenish as described in Sections 5.2 and 5.8
- **Relative oxalate concentration**
  Determine as described in Section 6.1 and
  Replenish as described in Sections 5.2 and 5.8
- **pH**
  Determine and correct as described in Section 5.8
- **Discoloration and clouding of dye solution**
  Correct as described in Sections 2 and 3.

If these measures are not adequate or if ferrooxalate is present in the bath (positive ferrooxalate identification as described in Section 6.2), add oxalate and hydrogen peroxide as described in Section 5.8.

Note
These recommendations, especially the analysis specificatons, are based exclusively on the specific properties of **Sanodal Gold 4N** and do not apply to normal commercial ammonium ferrioxalate.