

Sanodal[®] Deep Black MLW

Recommendations for its application and the operational maintenance of the dyebath

Sanodal Deep Black MLW dyeings have for many years set a standard for quality in the finishing of aluminium products generally and of exterior architectural aluminium in particular.

This technical information bulletin contains recommendations covering the optimum conditions of application and the upkeep of the dyebath, together with pointers to possible causes of faulty dyeings and suggestions for their prevention.

Sanodal Deep Black MLW is used mainly for the production of black dyeings in two sectors:

- aluminium products and components for which weathering fastness is not a major requirement, e.g. housewares, optical instruments, indicator plates, articles for interior decoration
- exterior building elements of high weathering fastness.

The following recommendations for its application and the maintenance of the dyebath apply for both these sectors of production.

1. Dyestuff Specific Data

Physical form:	fine powder
Chemical character:	Azo dyestuff, heavy metal complex
Specific weight:	ca. 800 g/l
Solubility in water:	ca. 50 g/l (20°C)
Storage stability:	practically unlimited; close the packaging well after use.
Ecological and toxicological data:	see safety data sheet.

2. Finishing conditions

	Concentration	Dyeing temperature	Dyeing time	pH
Standard anodized layers thickness (12 µm)	10 g/l	55 – 60°C	10 – 20 min	4,5
Sanodal anodized layer thickness (25 µm)	10 g/l	55 – 60°C	30 – 45 min	4,5

2.1 Setting the bath

We recommend to dissolve the dyestuff in demineralized water. Tap water is suitable as well, but the bath stability can be reduced, however.

The powder dyedstuff should be completely dissolved before addition to the bath. It is best to paste it with some hot water, stirring constantly until a homogeneous paste free from lumps is formed, and then to add more hot water with continued stirring so that the paste goes slowly into solution. In all about 5 parts of water to 1 part dyestuff is necessary.

As a check to make sure the dyestuff is fully dissolved, it is a good practice to run the prepared solution through a fine gauze or wire-mesh filter.

In order to optimise the colouring properties of the dye bath, boil the bath for a short time (approx 1 min) or keep the bath at a temperature of 60 °C (140 °±) for 4-5 h before dyeing.

2.2 pH of the dye bath

The optimum value for dyeing and stabilisation of the dye bath is pH 4.5 (see section 4).

It is advisable to correct pH deviations

- on the acid side with dilute formic acid (dilute sulphuric acid has a less favourable effect)
- on the alkaline side with dilute caustic soda solution.

The life of the bath is shortened by pH values beyond the tolerance region of 4.0 – 4.8 owing to accumulation of aluminium (section 6.1) or ageing (section 5). Moreover lower pH values encourage bronzing of the dyeing (section 9.1).

2.3 Dyeing temperature

The optimum temperature for build-up of the dyestuff is 55 – 60°C.

At the lower temperatures, e.g. room temperature, a smaller amount of dyestuff is adsorbed in the anodic coating in constant dyeing time. Extending the time increases the amount taken up by the coating, although the final amount is not equal to that adsorbed in dyeing at 60°C.

Dyeings produced at lower temperatures are easier to strip (an important point for the manufacture of name plates), but they bleed rather more heavily in the sealing solution.

At temperatures above 60°C the amount of adsorbed dyestuff decreases and cannot be increased by extending the dyeing time.

2.4 Dyeing time

Under the normal anodising and dyeing conditions, i.e.

- coating thickness 12 – 15 µm
- dyeing temperature 60°C
- pH 4.5
- dye concentration 10 g/l

the saturation limit is very nearly reached after dyeing for 20 min. Longer dyeing times do not result in any significant increase in the intensity.

On the thicker or denser (harder) coatings and at lower temperatures, the saturation point is not reached until after dyeing for longer than 20 min.

If the dyebath has been in use for some length of time it may be necessary to dye longer than 20 min and at a temperature of 60°C.

2.5 Sealing

The dyed oxide films must afterwards be sealed according to the guidelines for anodized aluminium, above all in the presence of **Anodal® SH-1 Liquid** or **Sealing Salt ASL**.

3. Light fastness of the dyeings

Sanodal Deep Black MLW is distinguished by its excellent light fastness.

Light fastness of **Sanodal** dyeings: rating > 9 (ISO 2135).

4. Stability of dyebaths

Given proper attention, **Sanodal Deep Black MLW** dyebaths can be kept in service for months or even years without any falling off in the dyeing capacity. However the following conditions are essential:

- the dyeing tank or vessel should be made of a suitable material such as refined steel, earthenware or a speciality plastic
- during storage the bath should be held at a pH below 5 to minimise “natural ageing”
- foreign substances which interfere with dyeing should as far as possible be screened out (see section 6.)
- the bath pH should be checked periodically and corrected with formic acid or sodium formate

(see section 2.2).

The life of dyebaths is reduced by

- water containing phosphates, e.g. chemically softened water
- entrained foreign matter (see section 6.).

5. Ageing dyebaths

In the course of months or years a dyebath may age, even if it has not been used for dyeing. This is reflected in lower building-up capacity at constant concentration due to decreased dye activity.

The natural ageing process can be retarded by taking the following precautions:

- shield the bath from the action of light and air
- keep the bath at room temperature when not in use
- check the pH at regular intervals and maintain the value between 4 and 5 (see section 4.)
- after every lengthy break in dyeing such as occur in the operation of the **Sanodal** System, check the concentration and activity and if necessary strengthen the bath (see section 7.).

6. Introduction of foreign substances (contaminants)

If foreign ions are introduced and accumulate in the dyebath, the power of build-up of the dyestuff may diminish and dye precipitates may be formed.

The following foreign ions cause interference:

<i>Al</i>	partly drawn in from the anodising bath and partly set free in the dyebath itself (see section 6.1).
<i>Fe</i>	(rust) occurs as an impurity in untreated water and through corrosion of the dyeing tank and fittings if these are made of unsuitable material.
<i>Nitrates</i>	from the nitric acid treatment.
<i>Sulphates</i>	from the anodising bath.
<i>Phosphates</i>	from chemically treated water and the desmutting bath.
<i>Ni, Co, Sn, Cu</i>	from electrolytic dyebaths.

6.1 Metalions

Aluminium ions tend to be carried into the dyebath inadvertently, even when the anodised aluminium is rinsed before dyeing. If the pH is too low during dyeing, Al may also be formed through partial dissolution of the anodic coating. Aluminium not only reduces the power of build-up and causes precipitate formation but also makes it difficult to clear any film formed by partial drying when the aluminium goes into the following rinse water. This can induce bronzing of the dyeing (see section 9.1).

The aluminium content of the dyebath should therefore be kept as low as is practicable. This condition can be met by rinsing the anodised parts thoroughly before entry. Two-stage rinsing gives good results, especially when combined with an intermediate standing rinse bath of deionised water. The pH of the rinse waters should not be lower than 4.

No aluminium, iron, copper or other metal objects should be left lying in the dyebath.

6.2 Oily surface film on the dyebath

If a dyebath has been left standing for several weeks without being used or agitated, an ultrafine oily film may build up on the surface. It may be formed by oil particles from unfiltered compressed air or by minute precipitates in the bath itself. Such a film can easily lead to cloudy dyeings or smudge on the metal surface. To prevent formation of this undesirable film the following steps should be taken:

- use filtered compressed air free from oil
- agitate the bath vigorously from time to time.

7. **Strengthening, partial renewal and re-setting of dyebaths**

It is advisable to carry out bath control by determining the dye concentration and the activity, as is the practice in the **Sanodal** System*

*See brochure **Sanodal** for producing light and weather-fast dyeings on anodized aluminium building components”.

Depending on the state of the bath, one of the following measures will be necessary:

- strengthening
- partial renewal
- re-setting.

7.1 **Strengthening**

This is carried out at the latest when the actual concentration has fallen 10 % below the set concentration. The bath should also be strengthened if its activity has declined. In this case the loss in activity must be offset and the consumed dyestuff replaced as well, which may mean that the amount added will raise the concentration above the initial level.

7.2 **Partial renewal**

This modified form of strengthening is carried out preferably when the actual concentration is significantly higher than the initially set concentration owing to a high content of foreign ions, i.e. when the bath activity has diminished.

Although this calls for uneconomically high additions of fresh dyestuff, they are necessary to reach the required dyeing capacity.

In such cases “regeneration” of the bath by partial renewal has proved effective.

A part of the old bath (until 50%) is reject and replace by a new bath with 10 g/l dyestuff.

This partial renewal method has the following advantages:

- the dye concentration remains within acceptable limits for dyeing over a long period of time
- dilution cuts down interference effects from foreign substances
- the working life of the bath is prolonged which eases the effluent treatment situation.

7.3 **Re-setting bath**

If the bath activity falls to below 70 %, i.e. if a tentative partial renewal proves uneconomic, a fresh bath has to be set.

8. **Clarification of dyebaths**

Although dissolved foreign substances may depreciate the dyestuffs power of build-up, they do not affect the levelness of the dyeings. Should any variations in intensity appear they are traceable to lack of homogeneity in the anodic coating or in the dyebath. Normally suspended solids (precipitates and other contaminants) are not important unless they remain adhering to the aluminium, in which case they may be visible later as fine specks.

Resinous and oily precipitates are much more damaging because their consistency and low specific gravity enable them to accumulate on the bath surface to form a more or less continuous film. This contaminates the aluminium and produces conspicuous specking.

8.1 Removal of solids

Precipitation and other solids can be removed from the bath by filtration.

The filter units used for the clarification of electroplating baths, which have pore sizes of 8 – 15 µm, have given good service.

Activated carbon filters should not be used since the carbon absorbs dyestuff, thereby reducing the concentration and hence the dyeing power of the bath.

8.2 Removal of oily films

It is not always possible to prevent formation of an oily film on the bath as described in section 6.2. In the industry it has been found that vigorous agitation of the dyebath from time to time is effective in inactivating the film. Often the build-up of an oily film can be prevented by adding a small amount of a nonionic wetting agent, e.g. <0.1 g/l **Ekaline F Liquid**. If this is not successful the thin, barely visible film should be removed.

This can be done by picking it up on absorbent paper, e.g. dry newsprint, or with a charge of oil-absorbing cubes, pellets, flakes, etc.

9. Other causes of faulty dyeings

Even when the recommendations made in sections 2 and 4 are observed, under certain conditions interference effects may occur, the reasons for which are not immediately evident. Such faults include bronzing of the dyeing and galvanic pitting corrosion on the dyed aluminium.

9.1 Bronzing of dyeings

The brownish bronze effect on dyed aluminium may be a thin abradable film or abradable specks; it is particularly liable to occur on rough and dull aluminium surfaces.

Bronzing is due to the following factors:

- Incorrect bath pH

At pH values of < 4, under otherwise correct conditions an uneven bronzing effect may appear. For this reason the pH should invariably remain between 4.2 and 4.8 (see section 2.2).

- Excessive aluminium content – Partial drying of adsorbed solution

When the dyed aluminium is raised for transfer to the next bath, the adhering dye solution may partially dry to form an extremely fine film of solids. This film is bronze in colour and can be wiped off or rinsed off. But as the aluminium content of the dyebath increases the water solubility decreases, making the film increasingly difficult to remove in the rinsing water. Thorough rinsing of the anodised aluminium prior to dyeing, from the moment a freshly prepared dyebath goes into use will very largely prevent the rise of conditions leading to bronzing.

If in spite of this precaution bronzing appears on dyed parts after a certain time, the pH of the bath should be re-adjusted to the optimum value. If this does not solve the problem, the bath needs renewing. When the fresh bath is set it will of course be adjusted to the optimum pH, and from this point on the anodised parts should always be rinsed well before entry.

9.2 Galvanic corrosion

Should the frames and holding clamps be made of titanium instead of aluminium, they may leave small indentations at the edges of the parts with undyed surrounding areas. At these points there is a danger of pitting corrosion.

Pitting corrosion can be brought about by the combined action of minute amounts of a corrosive electrolyte such as common salt on the one hand and weak galvanic currents on the other. In contrast to aluminium which is sheathed in an electrically insulating oxide coating when anodised, titanium connects the metal dye vessel in a circuit with the aluminium that is being dyed, giving rise to galvanic currents and hence corrosion. This may take place in dyeing with **Sanodal Deep Black MLW**, although its content of corrosive salts (chlorides) is extremely low.

As a rule galvanic currents can be eliminated by insulating the holding frame against the dyeing tank, or by installing dye vessels made of a nonconductive material such as plastic or hard rubber.

9.3 Mould formation on the bath

Given unfavourable ambient conditions, mould may grow on the surface of the bath. If a mould film is picked up by the anodised aluminium it will act as a resist and prevent build-up of dyestuff on the affected areas.

Controlling mould formation

- Skim off the mould film
- Raise the dyebath to 90°C/194°F and hold this temperature for a short time which will kill most of the mould spores
- Addition of 0.02 – 0.05 g/l of the biocid Saniprot 98-70 from
SANITIZED Marketing AG
Lyssachstrasse 95
CH-3401 Burgdorf

10. Treatment of spend dyebaths

Spend dyebaths have to be treated, for example with **Anodal WT-1 liquid**. In the technical information of **Anodal WT-1 liquid** the precipitation process is described in detail.

The table below shows the necessary dosing concentration for the precipitation of **Sanodal Deep Black MLW**.

Precipitation method	FeCl ₃ 40 % ml/g dye	Etching lye ml/g dye	Anodal WT-1 liquid ml/g dye	Residual dye in the filtrate mg/l	Chrome content in the filtrate mg/l
A	1,8	-	0,8	< 1	< 0,05
B	1,8	-	0,8	< 1	< 0,05
C	-	1,8	0,8	~ 1,5	< 0,05

Many of their dyestuffs, pigments and chemicals are patented by Clariant Ltd. or its affiliates in numerous industrial countries.

® Trademark registered by Clariant Ltd or Clariant GmbH in numerous countries.

* Trademark licensed to Clariant Ltd in numerous countries.

+ Manufacturer's registered trade mark.

The signs ®, * and + appear only at the first mention of the product.

The information and recommendations presented here were compiled with the utmost care, but cannot be extended to cover every possible case. They are intended to serve as non-binding guidelines and must be adapted to the prevailing conditions.