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METHOD FOR THE BLACKENING OF ALUMINIUM

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ABSTRACT OF THE DISCLOSURE

An even, tenacious black coating of nickel sulfide is applied to the surface of aluminium alloys by immersion of the alloy into an aqueous bath containing from 35–200 g./l. of $NiCl_2.6$ aq and from 0.03–0.25 molar of thiocyanate ions for a period up to 5 minutes according to the process disclosed. Preferably the aqueous bath also contains from 10–20 g./l. of NH_4Cl, from 8–12 g./l. of KCNS and is maintained at a pH in the range of 3–4.

The invention relates to currentless blackening of aluminium alloys by immersion in a blackening bath.

It has been found that according to the known methods of currentless backening the aluminum alloy 7075, known as perunal, cannot be properly blackened.

The aluminium alloy 7075 is stated as follows in regard to composition:

Cu	1.3–1.8
Si(Fe+Si)	Max. 0.4
Mn	0.1–0.4
Mg	2.1–2.5
Zn	6.0–6.5
Cr	0.1–0.3
Ti	0.03–0.15

The specific gravity is 2.80.

By properly blackening is meant, in connection with the above, applying a black coating to the aluminium, which coating satisfies the undermentioned four requirements:

(1) The emission coefficient of the coating must be greater than or equal to 0.8 for temperature radiation between 20° and 100° C.
(2) As a criterion for adhesion the coating must be able to pass a tape test.
(3) The coating should be very even.
(4) The cost of applying the black coating should be very low.

The invention aims at providing a method for applying a good black coating; to aluminium alloys, which coating will satisfy the aforementioned four requirements.

According to the invention a blackening bath is used with the following concentrations and conditions:

$NiCl_2.6$ aq g./l.	35–200
Concentration of ammonium ions molar	0.12–0.40
Concentration of rhodanide ions do	0.03–0.25
Bath temperature ° C.	40–90
Immersion time minutes	½–5

Not only the alloy perunal but also other aluminium alloys, as for instance the following alloys known at present under the code designations Al 6061 and Al 2 S, can be provided with a good covering by means of the above-mentioned blackening bath.

The ammonium and rhodanide ions may be added to the blackening bath as ammonium rhodanide (NH_4CNS).

In many cases, however, the rhodanide is added to the blackening bath in the form of an easily soluble alkali metal rhodanide, and the ammonium ion in the form of NH_4Cl.

A blackening bath that gives good results for the blackening of perunal is the following bath with the indicated concentrations and bath conditions:

$NiCl_2.6$ aq g./l.	65–85
NH_4Cl g./l.	10–20
KCNS g./l.	8–12
Temperature ° C.	70–80
pH	3–4

The pH of a freshly prepared blackening bath is approximately 5. For good blackening the pH should as a rule be from 3 to 4. It has been found that with a freshly prepared bath some difficulties may at first occur in applying the black coating, coinciding with a period in which the pH of the bath drops from 5 to a constant value of approximately 3.5.

This pH drop is most probably caused by partial hydrolysis of aluminium ions dissolved in the bath during blackening and by the formation of H_2S.

These initial difficulties with a freshly prepared bath can be avoided by adding $AlCl_3.6$ aq to the bath. The bath concentration of the $AlCl_3.6$ aq is from 0.5–2 gl./l.

The aluminium, blackened in a black-colouring bath, shows after rinsing in water and optionally demi-water a white efflorescence on being dried in air. This is probably due to an after-reaction of the aluminium basic material (underneath the black, porous coating) with the bath liquid still present in the pores.

The reaction product appears on the black coating as white spots which can be removed by being rubbed with a dry cloth. The efflorescence causes the blackened aluminum to become greyer. This drawback can be obviated by giving the blackened aluminium an after-treatment bath, as a result of which the after-effect is checked. This also results in better adhesion of the black coating than is obtained in cases where the after-effect has not been checked.

A good after-treatment is that of immersion in a bath having the following concentrations and bath conditions:

Potassium bichromate g./l.	15–25
50% nitric acid ml./l.	5–15
Temperature	Room temperature
Immersion time minutes	1–3

It is observed that the potassium bichromate may be entirely or partly replaced by an equivalent quantity of some other cheap alkali bichromate.

Another form of after-treatment which, if possible, gives even better results than the treatment previously mentioned, is immersion in a bath having the following concentrations and bath conditions: alkali nitrate corresponding to

Potassium nitrate g./l.	15–100
Immersion time minutes	1–15
Temperature ° C.	10–60

Preference is given to immersion in a bath containing alkali nitrate, the bath conditions being as follows:

Potassium nitrate g./l.	25–50
Immersion time at room temperature minutes	5
Immersion time at 50° C. do	2

The invention is elucidated below in three detailed examples in which a number of test plates of perunal with a perunal thickness of 4 mm. and dimensions of 5 x 2 cm. are successively pretreated, blackened and after-treated.

The pretreatment usually consisted in the following forms of treatment:

(1) removal of grease
(2) rinsing in water for 0.5 minute
(3) alkaline pickling
(4) rinsing in water for 0.5 minute.

If the perunal was already properly clean and grease-free, treatments 3 and 4 only were carried out.

The after-treatment consisted in rinsing in water, followed by counteraction of efflorescence by bichromate/nitric acid or alkali nitrate baths, again followed by rinsing in water and drying.

The removal of grease was effected in a grease-removing bath having the undermentioned composition and bath conditions:

Sodium gluconate	g./l.	150
Trisodium phosphate	g./l.	50
Temperature	° C.	80
Bathing time	minutes	5

Alkaline pickling was effected under the following conditions:

Sodium hydroxide	g./l.	50
Sodium gluconate	g./l.	100
Temperature	° C.	60–70
Bathing time	minutes	1–2

As a result of alkaline pickling a black, non-adhesive coating of residual alloy elements is produced on the perunal plates.

When the (non-adhesive) black film resulting from alkaline pickling has been formed in a good, even manner over the entire surface, it is certain that the entire surface is active and that the pretreatment has been sufficient.

Example I deals with experiments which resulted in the determination of a blackening bath containing the optimum concentrations of $NiCl_2.6H_2O$, NH_4Cl and KCNS.

Example II deals with the after-treatment of blackened perunal plates with a $K_2Cr_2O_7/HNO_3$ bath.

Example III deals with after-treatment with a KNO_3 solution.

EXAMPLE I

In the following series of experiments the optimum concentrations of the above-mentioned three bath components, with to working conditions, was broadly determined.

(1) The optimum concentration of nickel chloride

In a solution of 30 g./l. of ammonium chloride with 20 g./l. of potassium rhodanide, test plates were blackened at 75° C. (and subsequently also at lower temperatures), the bathing times being from 1 to 2 minutes, whilst the nickel chloride content was increased as follows:

g./l. $NiCl_2$ 6 aq.: 0–25–50–75–100–150–200–300–400

At 0 and 25 g./l. of $NiCl_2.6$ aq, no reaction with the Al 7075 occurs at 75° C.; there is no gas development nor blackening.

From 25–50 g./l. of $NiCl_2.6$ aq the Al plates does get blackened, but no even film is produced.

From 50–150 g./l., good, black, adhesive deposits are obtained. Between 150 and 400 g./l. of $NiCl_2.6$ aq the reaction of the aluminium with the liquid becomes increasingly vehement, whilst above 200 g./l. of $NiCl_2.6$ aq there is a tendency for pure nickel to be deposited, as a result of which a greyer appearance is obtained. Owing to the vehement reaction the bathing time must be kept very short, but in spite of this the phenomenon of after-reaction during drying is very pronounced. Summarizing, it may be stated that the optimum nickel chloride concentration lies between the limits of 50–150 g./l. in a bath containing 30 g./l. of ammonium chloride and 20 g./l. of potassium rhodanide.

(2) The optimum concentration of ammonium chloride and potassium rhodanide

The initial composition selected is as follows:

$NiCl_2.6$ aq	g./l.	300
KCNS	g./l.	20
Temp.	° C.	75

In this composition test plates (about 5) were blackened until, owing to lack of ammonium chloride, a black finish was no longer obtained.

After this 15 g./l. of NH_4Cl was added, so that the bath was now composed as follows:

$NiCl_2.6$ aq:300 g./l.
KCNS:20 g./l.
NH_4Cl:30 g./l. } ---------- 75° C.

The plates treated in this bath all become grey and show pronounced efflorescence. This result agrees entirely with the results under 1, in which with high nickel concentration no more blackening was obtained either.

The ammonium chloride content was subsequently increased to 30 g./l. and then to 60 g./l., whilst the rhodanide content was brought 40 g./l. Good blackening was not obtained with this nickel content. After this the blackening bath was diluted 1:1, as a result of which the following composition was produced.

$NiCl_2.6$ aq:150 g./l.
KCNS:20 g./l.
NH_4Cl:15 g./l. } ---------- 75° C.

With this bath fairly black deposits were obtained, although the blackening was not optimum. A second dilution yielded the following bath:

$NiCl_2.6$ aq:75 g./l.
KCNS:10 g./l.
NH_4Cl:15 g./l. } ---------- 75° C.

The plates treated acquire very good blackness in this bath; the best results are obtained with short immersion times (about 1 minute).

Next, the bath was again diluted 1:1:

$NiCl_2.6$ aq:35 g./l.
KCNS:5 g./l.
NH_4Cl:7.5 g./l. } ---------- 75° C.

The test plates became properly black in the above bath, and the brief immersion times of 1 minute again gave the best results. To this bath 7.5 g./l. ammonium chloride was added, and the results remained good. After this 15 g./l. of KCNS was added, giving the composition:

$NiCl_2.6$ aq:35 g./l.
KCNS:20 g./l.
NH_4Cl:15 g./l. } ---------- 75° C.

With this bath, too, very good results were obtained. The ammonium chloride content was subsequently increased to 30 g./l. and subsequently to 60 g./l.

At 30 g./l. the plates still became reasonably black, but a greater white efflorescence occurred during drying in air.

A content of 60 g./l. of NH_4Cl proved too high to obtain blackening: the plates become grey in appearance and show much white efflorescence on drying. Increases of the nickel chloride content to 75 g./l. hardly improved matters. The ammonium chloride content was afterwards further increased from 60 g./l. via 120 g./l. to 180 g./l., with the result that the test plates became increasingly grey and showed more white efflorescence on drying.

The results of this examination of the composition of the blackening nickel bath may be summarized as follows:

The nickel content of the bath is not so very critical. Depending somewhat upon the ammonium chloride concentration, good results are obtained with a nickel content corresponding to 35–150 g./l. of $NiCl_2.6H_2O$. Below this lower limit the test plates react very little, if at all, at 75° C. or lower. A possible blackening is then only local. Above the upper limit of 150 g./l. of $NiCl_2.6$ aq grey deposits (mainly nickel) are generally produced.

The ammonium chloride content is critical. Depending somewhat upon the nickel content, good results are obtained within the range: 7.5–30 g./l. of ammonium chloride. A deficiency of ammonium chloride has the effect that a new bath yields no more blackening after a few test plates.

Too high an ammonium content results in a grey deposit which, moreover, shows on drying a great deal of white efflorescence causing additional difficulty in the after-treatment. The reaction of the test plates with the liquid is accelerated by additions of ammonium chloride.

The potassium rhodanide content is not critical. Good results were obtained within the range 5–20 g./l. of KCNS. Too low a content of potassium rhodanide or absence of KCNS prevents the formation of a black coating (grey appearance).

A very high rhodanide content intensifies the reaction of the test plates, as a result of which short bathing times have to be selected.

The bath temperature is not very critical. Good results were obtained in the range of 50°–90° C.

The reaction becomes more vehement according as the temperature rises, as a result of which shorter bathing times have to be selected.

At lower temperatures and with longer bathing times the effect of bad coverage is more likely to occur: it is then more difficult to get the test plates equally black over their entire surface.

Acidity of the bath. A newly-prepared bath has a pH of about 5. After a few test plates this pH drops to a value of from 3.5 to 4 and then continues constant. In all probability this pH drop is the result of the formation of H_2S and partial hydrolysis of the $AlCl_3$ formed.

The bathing time is critical. The short bathing times give rise to bad coverage, no even blackening. Too long bathing times gives the test plates a greyer appearance. Depending upon the bath temperature and composition, the bathing time may vary from 0.5 to 3 minutes. Other alloys than 7075 (for instance 6061) must have somewhat longer bathing times as compared with 7075. It may be stated in general that the less the aluminium is alloyed the more vehement the reaction and the longer the bathing time to be selected.

The following may be said about the reaction mechanism:

During the blackening of Al 7075 a distinct H_2S smell was perceptible, whilst after blackening there was also a slight smell of prussic acid.

Analogous to this, the following overall reaction equation would be applicable to the blackening of aluminium:

$$2Al+3NiCl_2+KCNS \rightarrow 2AlCl_3+KCN+3NiS$$

The pH drop can be accounted for by the acid reaction of $AlCl_3$ by hydrolysis to $Al(OH)_3$.

As regards the part played by aluminium chloride, it would seem likely that during blackening a high pH is produced locally on the surface as a result of the dissolving of aluminium.

The ammonium ion may then counteract the production of $Ni(OH)_2$ and thus promote formation of black NiS.

Actually, if one started with NH_4CNS instead of KCNS, the bath might just as well be made up of two components, as it is not the chloride ion from NH_4Cl that is essential (this ion being of course sufficiently available in $NiCl_2$), but the ammonium ion.

The composition limits of the blackening nickel bath may from the foregoing be stated as follows:

$NiCl_2.6$ aq:35–150 grams opt. 75 g./l.
NH_4Cl:7.5–30 grams opt. 15 g./l.
KCNS:5–20 grams opt. 10 g./l.
temperature:50–90° C. opt. 75° C.
pH:3–4

The pH of a new bath is about 5. It was found that some difficulties may occur at the start in obtaining coverage of the black coating, corresponding to the period in which the pH of the bath drops from 5 to a constant value of about 3.5.

One of the possibilities is to bring a newly-prepared bath beforehand up to a pH of 3.5 by adding $AlCl_3$ (±1 g./l. $AlCl_3.6$ aq). In practice such artificial "maturing" of the bath may be of service for the avoidance of possible initial difficulties in production.

EXAMPLE II

The perunal plates, provided with a black coating in the blackening bath according to Example I, were subjected to the following treatment in an after-treatment bath.

$K_2Cr_2O_7$	g./l.	20
50% nitric acid	ml./l.	10
Bathing time at 50° C.	minutes	1
Bathing time at room temperature	do	1–3

The appearance of the plates is somewhat greyer than in Example III; a pretreatment in which the black pickling coating is not removed and blackening is effected with this coating after rinsing in water in the blackening nickel bath according to Example I, does, however, give a sufficiently black plate.

EXAMPLE III

In this example the preunal plates were treated as follows:

KNO_3	g./l.	25–50
Bathing time at room temperature	minutes	5
Bathing time at 50° C.	do	2

The appearance of the plate is properly black, whilst adhesion in general is somewhat better than in Example I.

In both cases it will suffice to effect a simple rinsing of 1–2 minutes after the pretreament bath. A possible short dip (max. 30 sec.) in hot demi-water (max. 50° C.) speeds up drying in air but is not essential to the apearance of the aluminium. Lastly, it may be observed that by excessively long pretreatment of the aluminium (heavy pickling) and long bathing times in the blackening bath (more than 2 minutes) the surface of the aluminum becomes rough and more porous. The aluminium processed in this way has a strong tendency towards white efflorescence and renders after-treatment difficult.

We claim:

1. A method for currentless blackening of aluminum alloys comprising immersing said aluminum alloy for about 0.5 to about 5 minutes in an aqueous bath which contains 35–200 g./l. of $NiCl_2.6$ aq and 0.03–0.25 molar thiocyanate ions, the bath temperature maintained at about 40 to about 90° C.

2. The method as claimed in claim **1** wherein said aqueous bath consists essentially of $NiCl_2.6$ aq 65–85 g./l., NH_4Cl 10–20 g./l. and KCNS 8–12 g./l., said bath maintained at a temperature of about 70 to about 80° C. and at a pH of about 3 to 4.

3. The method as claimed in claim **1** wherein $AlCl_3.6$ aq in a concentration of 0.5–2 g./l. is included in said aqueous bath.

4. The method as claimed in claim **1** including the additional step of immersing the thus-blackening aluminum alloy in an aqueous bath containing potassium bichromate 15–25 g./l. and nitric acid (50%) 5–15 ml./l. at ambient temperature for a period of about 1–3 minutes.

5. The method as claimed in claim 1 including the additional step of immersing the thus-blackening aluminum alloy in an aqueous bath containing potassium nitrate 15–100 g./l. at a temperature of about 10 to about 60° C. for a period from about 1 to about 15 minutes.

6. The method as claimed in claim 5 wherein the potassium nitrate concentration is 25–50 g./l. and the immersion time is from about 5 minutes at room temperature to about 2 minutes at about 60° C.

7. A method of applying an even, tenacious black coating on aluminum alloys in the absence of current, said coating having an emission coefficient of at least 0.8 for a temperature radiation between 20° C. and 100° C., comprising immersing said aluminum alloy in an aqueous bath consisting esentially of:

	G./l.
NiCl.6 aq	65–85
NH_4Cl	10–20
KCNS	8–12

at a temperature of about 40 to about 90° C. and at a pH in the range of about 3–4.

8. A method of applying an even, tenacious black coating on aluminum alloys in the absence of current, said coating having an emission coefficient of at least 0.8 for a temperature radiation between 20° C. and 100° C., comprising immersing said aluminum alloy in an aqueous bath which contains 65–85 g./l. of $NiCl_2.6$ aq, 10–20 g./l. of NH_4Cl and 8–12 g./l. of an alkali metal thiocyanate or ammonium thiocyanate at a temperature of about 40 to about 90° C. and at a pH in the range of about 3–4.

9. A blackened aluminum alloy article having an even, tenacious black coating of nickel sulfide thereon, said coating having an emission coefficient of at least 0.8 for a temperature radiation between 20° C. and 100° C., applied according to the method of claim 1.

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