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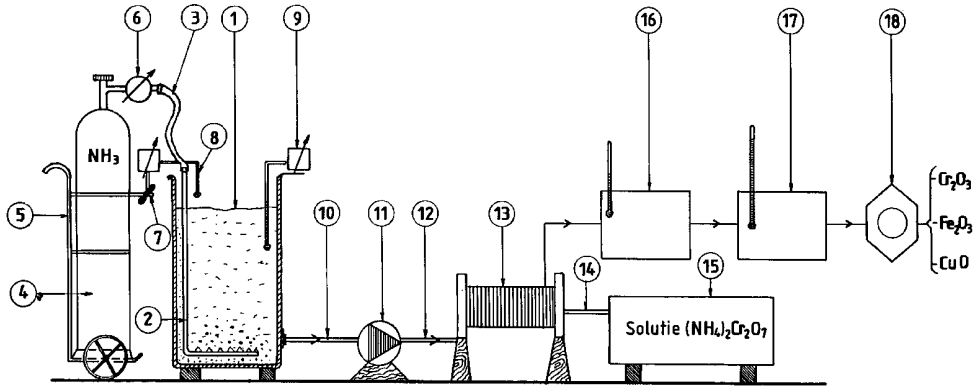
(54) **Title:** METHOD AND INSTALLATION OF METAL RETRIEVING FROM USED CHROMING SOLUTIONS



(57) **Abstract:** The invention concerns a method or procedure and an installation of metal retrieving from used water chroming solutions, with high content of Cr and other impurifying metals as Fe, Cr^{3+}, Cu, using as reactive the gas ammonia, introducted at the base of the reaction tub, through a detachable device, connected to a gas contained through a flexible tube. The technology consists in the reduction of the acidity of the used solution, from PH = 0,5 to a PH of 5.5, in the same time with the precipitation of the impurifying metals as insoluble hydroxydes non toxic and re-usable, as well as the separation of the Cr^{6+} as water solution of ammonia dychromate.

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METHOD AND INSTALLATION OF METAL RETRIEVING FROM USED CHROMING SOLUTIONS

The invention concerns a method and an installation of retrieving metals after the neutralization of the used water chroming solution, proceeded from the chroming bath of pieces made from ferrous or non-ferrous materials.

In the field of protection covering,a place of it`s own is occupied by the functionnal and protecting - decorative depositions made by dure chroming. During the anodic attack of the pieces to be chromed into the solution are passing metalic ions from the superficial layed that can be iron,copper, zinc,nickel and others. Also in this solutions there are forming ions of Cr^{3+} by reduction of Cr^{6+} at the cathode. The iron and Cr^{3+} in this concentration improve the covering capacity of chroming solution. It has been proved that the sum of $Fe + Cr^{3+}$ must not exeed 20 g/L value over which the efficiency of the processus is decressing and the chroming solution is considered worn ou

There are methods of neutralization and retrival of metals from a solution of chroming that is used,methods consisting either in the trea ment with reactives of precipitation of Cr^{6+} as insoluble chromats, using barium salts or lead salts,or the separation of Cr^{6+} from the other metals with the help of the ion changer or by electro-dyalisis.

The drawbacks of these methods consist in the neutralization of the solution of chroming used in order to purify the residual waters to be eliminated.

In this manner, result abundant muds that imply either adequate storage or use of expensive toxic reactives, requesting precise dozing in order

to avoid any excess.

There are also in use some installations of treating the water chroming solution consistiong in an umique vessel of neutralization within the treating station of galvanic water.

The drawbacks of these installations consist in those that they are ment for the diluted water solutions,steo-chiometrically treated after chemical analysis,with a requirement of adequate space for waste deposit.

This technical obstacle our invention avoids consists in the retri eval from the water used chroming solutions of both the active metalic element that is Cr^{6+} and the impure metalic elements.

Our technical procedure avoids the drawbacks hereby described by permitting the treatment of the water solution of chroming that has been used,containing Cr^{6+}, Cr^{3+}, Fe as other heavy impure metals as Zn, Cu,Cd, Ni,Al,came from the anodic attack of the pieces subject of the chroming process within environemental temperature - with gas ammonia 30 - 40 $1/cm^3$for a period of 1, - 1,5 Hours when the solution temperature reaches 75 - 80^{o} Celsius resulting a water solution of ammonia di-chromate and metal precipitation under a form of insolvable hydroxides,not toxical and re-usable in the same time with the reaction of neutralization when the PH reaches 5,5 - 6.

The installation, accordind to the invention, leaves aside the draw backs hereby mentioned by the detachable distributer made out of lead for gas Nh_3 placed inside and at the bottom of a tub, filled with used water solution,connected through a flexible tube to a gas bottle mounted on a carrige,with a electrochemical sensor of NH_3 as well as an aspiration pump to conduct the treated solution to a press-filter that separates the filtrated in a reservoir,and the resulted precipitate is dry,calcinated and ground.

The procedure and the installation,according to the invention, show the next advantages :

- permits the separate treatment of used chroming baths,
- permits the separation of the Cr^{6+} from the solution
- permits the recovery of the impure metalic elements as insolvable products,non-toxic and re-usable.
- dos not require toxic waste space.
- the construction is relatively simple,
- does not present any toxic hazard to the operator,
- does not afect the environemtnt

We hereby give an example of realization of the procedure and the installation,according to the invention, connected to the drawing representing a scheme - view of the technological processus.

The method, according to the invention, consists in treatment of water chroming solution that has been used, with a content of 150-160 g/l Cr^{6+}, 15 - 20 g/l Cr^{3+} ,15 - 20 g/l Fe and PH of 0,5 - 0,7 places in a metalic tub, placked inside with lead with gAS AMMONIA WITHIN A PRESSURE OF MINIMUM 35 AT, WITH A DEBIT OF 0,5 - 1 l /min, The ammonia consumption has been 30-40 l /m^3 time of 1 - 1,5 h and the initial temperature of the solution has been that of the environe ment. and final temperature of 75 - 80° Celsius, with PH at 5,5 - 6

The gas ammonia is a concentrated reactive,very solvable,with great difuzion power in water solution and a basic characteristic, reason for which it is used for the neutralization of the used water solution of chroming.

In the first step, there are forming NH_4^+ OH according to the reactic

$$NH_3 + H_2O \rightarrow NH_4^+ OH^- + Q1 \qquad (1)$$

that continues to react with the chromic acid according to reaction :

$$2HCrO_3^- \dashrightarrow Cr_2O_7^{2-} + H_2O \qquad (2)$$

$$Cr_2O_7^{2-} + Nh_4^+OH^- \dashrightarrow (NH_4^+)_2Cr_2O_7^{2-} + OH^- + Q2 \qquad (3)$$

This way, with the formation of the ammonia dychromate,there is a increase of the PH value from 0,5 to 5.5 or 6. Both the solubilization of

NH_3 and the reaction of the solution neutralization take place with great release of heat, reaching 75 - 80° Celsius,

In the second step of this processus, there is the reduction of the impure metals, consisting of Cr^{3+} Fe and Cu and the birth of a insoluble hydroxide mud within ph from 2,5 to 5,5.

The reaching of PH value of 6 and the presence of NH_3 at the surface of the solution indicates the termination of the reaction of neutralization and therefore cutting off the gas allimentation.
The excess of NH_3 has been avoided in order not to produce the solubilization of the precipitants formed as tetra amino-complexes and hexa amino- complexes.

Further on the solution treated as mentioned,is filtered, with the separation of the solution of $(NH_4)Cr_2O_7$ from the hydroxyde precipitat $Cr(OH)_3$, $Fe(OH)_3$,$Cu(OH)_2$.

The chemical analysis of the obtained filtrate has showed a con centration of : 195 -198 g/l of Cr^{6+} , 0,2 g/l of Cr^{3+}, 0,8 g/l Fe and 0,5 g/l Cu. As a result, an efficiency of Cr^{6+} recovery of over 95 %.

The mud resulted with a umidity of 15 - 20%, with 10-15% ammonia dychromate, is dryed at a temperature of 100 - 115° Celsius time of 5-6 Hours and is then calcinated at 500 - 6oo Celsius obtaining an conglomerate of metalic oxydes of Cr^{3+}, Fe and Cu.
The ammonia dychromate included in the mud is thermically decomposed by calcination according to the reaction :

$$(NH_4^+)_2Cr_2O_7^{2-} \dashrightarrow Cr_2O_3 + H_2O + N_2\uparrow \quad (4)$$

The installation for the retrieving of metals from the used chroming solution is composed from a distributor (2) mobile of gas ammonia, made out of lead and placed at the bottom interior of a lead plated tub. The distributor 2 is connected through a tube 3 flexible with an ammonia container with a pressure gauge 6, mounted on a push-kart

which sustains by a handler 7, an electrochemical sensor 8 for the ammon ia. The variation of PH value is indicated by a PH - meter 9, attached to the chroming tub 1.The evacuation of the treated solution is made with a aspiration pump 11, by pipes 10 amd 12, towards a Press-filter 13 The filtered material is retained in a reservoir 15 and the mud is put into a container 16 for drying and then calcinated in an oven 17 situated near a mill 18 with balls to grind the usual metalic oxydes to a granulation of maximum 30 u. The dust of Metalic oxydes may be used as pigment for an alchidic anti -rust grounding.

Example : Into the tub 1 there is a quantity of 1000 l solution (water chroming used) with temperature of the environement,with the fallowing composition : 200 g/l Cr^{6+} ,18 g/l Cr^{3+} ,12 g/l Fe, 5 g/l Cu and a ph of 0,5 treated with liquefied ammonia under a pressure of 35 AT from container 4,made with a valve and pressure gauge 6, mounted on a push-kart 5 for transportation. The gas ammonia has been introduced into the solution with the help of the distributor 2,from lead,pla ced at the bottom of the tub 1,with a debit of 0,8 l/min and connected t to container 4 by the flexible tube 3,a period of 70 min, to the obtaining of an PH of 5,8 indicated by the PH- meter 9,when the reactior of neutralization is practically terminated,signalized by the electrochemcal sensor 8 placed on the surface of the solution and attached to the handle 7 of the push-kart 5. The temperature in now reaching 78^{o} Celsius.

As fallows, the solution treated is vehiculated by the aspiration pump 11 by pipes 10 and 12 by the filter 13. The filtered material is collected into the retainer 15,in quantity of 860 l,had the fallowing composition : 198 g/l Cr^{6+} ,0,2 g/l Cr^{3+} ,0,8 g/l Fe, 0,5 g/l Cu and PH of 5,8.

The mud bread , composed of $Cr(OH)_3$, $Fe(OH)_3$, $Cu(OH)_2$ and with 10 - 15 % $(NH_4)_2Cr_2O_7$

and then dryed in theand container 16 at temperature of 110°Celsius a period of 6 hours and calcinated in the oven 17 at 600° Celsius. The conglomerate of metalic oxydes rezulted has been grinded in the mill 18 with balls untill reached granulation of 30 u and utilized as pigment in a anti- rust pre - painting.

CLAIMS

1. Method of metal retrieving from used chroming solutions,according to the invention,caracterised by the possibility of treatment of water solution containing 150-600gr/l Cr^{6+} ,15-20 g/l Cr^{3+} ,15-20 g/l Fe and other impuryfing metals as Zn,Cu,Cd,Ni,Al - came from the anodic attack of the pieces chromed within the limit of the environment temperature,with ammonia gas 30-40 l/m^3 at pressure of minimum 35 At. period of 1 - 1,5 h,when the temperature of the solution reaches 75-80°C,resulting a water solution of Ammonia dychromate and the precipitation of the impure metals as insoluble hydroxydes, non toxic and re-usable,in the same time with the reaction of neutralization when the PH reaches a value of 5,5 - 6, fallowed by an easy precipitation of the used metal at 100 - 115°C then calcination at 500 - 600°C and the final grinding to a granulation of max. 30 u of the resulted metalic oxydes.

2. The installation used to retrieve metals from the used water chroming solution.
With a mobil distributor (2) of gas ammonia,made out of lead,placed on the bottom - inside of a tub (1) made also from lead, connected through a tube (/) - flexible to a gas container (4) secured by a pressure gauge (6) mounted by a push-kart (5) with a NH_3 sensor on the handle (8) and(7) and the variation of the PH is indicated by a Ph - meter (9). The solution is handled with the help of a aspiration pump (11) by pipes (10 and 12) to a press - filter (13). The filtrated metal is collected in a container (15) and the conglomerate of precipitated is sent to an other container (16) for drying and then to a calcination oven 17 situated next to a ball grinder (18) for the grinding of the resulted metalic oxydes.

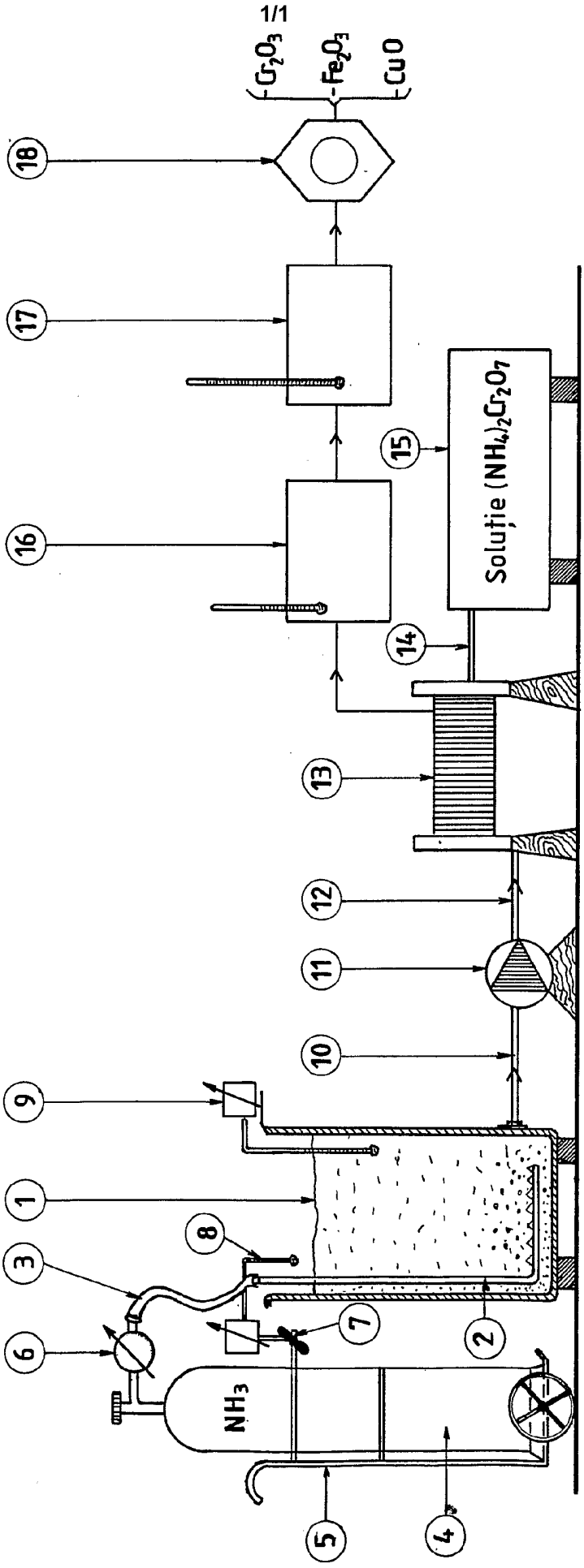
Cr_2O_3
Fe_2O_3
CuO
18
17
16
15
Soluție $(NH_4)_2Cr_2O_7$
14
13
12
11
10
9
1
8
3
6
7
2
NH_3
5
4

Fig. 1

INTERNATIONAL SEARCH REPORT

Inter al Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B34/32 C25D21/16 C25D21/18 C22B3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22B C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A		2
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A	FR 2 669 323 A (ISOCHROME) 22 May 1992 (1992-05-22) the whole document	1,2

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
17 January 2002	23/01/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Lilimpakis, E

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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