FLUORINE COMPOUNDS IN ELECTROFINISHING

N.V. Parthasaradhy

Central Electrochemical Research Institute Unit,
CSIR Complex, Madras 600 113.

INTRODUCTION

Fluorine is estimated to be the 13th in abundance of the elements. Simple and complex compounds, which are otherwise not widely used, have played important role in many facets of electrofinishing from aqueous media.

It is relevant to note that materials like aluminium alloys, magnesium alloys, zinc base alloys, stainless steels, the exotic materials such as Ti, Zr, Ta, Nb, W, Be, Ge, Si and Th, which are employed in strategic industries, rely on fluorine compounds for one aspect or the other of metal finishing. It is this aspect which gives a special place to fluorine chemicals in electrofinishing.

This review unfolds the fascinating contribution of the fluorine compouds.

IN CLEANING

Chloro-fluoro-hydrocarbons - trichlorofluoromethane [1], trichlorofluoromethane [2,3] are good degreasing agents [4], specially for metal-plastic combinations. They are particularly used for immersion cleaning of hermetically sealed motors, contacts, wiring, etc. A mixture of fluorocarbon solvent with methylene chloride, methanol (or ethanol) and cyclopentane or a mixture of different fluorocarbons as, for example, trichloro - trifluoroethane with smaller amounts of trichlor-monofluoromethane and tetrachoro-difluoroethane, are employed in electronics and precision metal working industries [5,6]. The solvent is suitable for cold cleaning as well as for vapour degreasing, the vapors being less toxic than even 1,1,1 - tri-chloroethane and look best when performance, safety, health, ecology and economy are considered [7].

FOR DESCALING

Metal finishers consider descaling or pickling as an important pre-plating sequence so that all foreign materials are removed from the substrate. While acids, individually or mixtures, generally satisfy this need for pickling common materials, in descaling special materails, the action of the picklers depend very much on the presence of one or the other fluorine compound.

For descaling stainless steel, after initial scale loosening in alkaline permanganate solution, it is dipped in HF bearing solutions of nitric acid with water/HCl/H_2SO_4 (or CrO_3 + H_2SO_4) (Table 1)

TABLE 1

DESCALING SOLUTIONS FOR STAINLESS STEEL

	H_2SO_4 ml	HNO_3 ml	HF ml	CrO_3 gms	HCl ml	Water	Temp
Sol 1	-	100	25	-	10	To	50-60
Sol 2	-	100	60	-	-	make	RT
Sol 3	60	-	60	60	-	one	≥ RT
Sol 4	80	160	20	-	-	litre	RT

To remove light scales from Ti, Zr, and Inconel alloy, HNO_3 - HF mixture is needed. For duralumin, NaF + H_2SO_4 solution is used followed by a dip in 50% by volume HNO_3 solution, while for cast iron HF + H_2SO_4 solution is used. A bright pickle for magnesium alloys consists of KF besides chromic acid and ferric nitrate.

Hot rolled low carbon steel has been descaled in HF 90 gpl or higher, with no inhibitor [8]. Although the rate of descaling is slow, substrate loss is considerably lower than in HCl or H_2SO_4 solutions. Similarly, HBF_4 solution (65-130 gpl) has enabled descaling of steel with very low loss of substrate material [9] (Table 2).

IN CHEMICAL POLISHING/BRIGHTENING

This process, if included in the finishing sequence, can reduce a few steps in mechanical polishing and enhance the overall surface finish of the component. Barrel technique for small components eliminates mechanical finishing completely. In the pretreatment cycle, if the surface of the job, after pickling, is

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TABLE 2

TO REMOVE LIGHT SCALES ON Ti IMMERSE IN

HNO_3	HF	Water	Temperature
250 ml	25 ml	to 1 litre	RT or higher

To clear the thin annealing scales on Zr loosen them initially in alkaline $KMnO_4$ and immerse in

HNO_3	HF	Water
1230 ml	100 ml	1230 ml

To clear **DURALUMIN** treat in

NaF	H_2SO_4	Water
10 gms	80 ml	to 1 litre

Followed by bright dip in 50% Vol. of HNO_3 solution

MAGNESIUM ALLOYS: A Bright Pickle Consists of -

CrO_3	$Fe(NO_3)_3$	KF	water
180 gms	40 gms	4 gms (2-7)	to 1 litre

CAST IRON: Immerse in

H_2SO_4	HF	Water	Temp.
125 ml	125 ml	to 1 litre	RT or higher

INCONEL ALLOY: Dip in -

HNO_3	HF	Water	Temp.
320 ml	40 ml	640 ml	65 - 75°C

LOW CARBON STEEL [8,9]:(Hot Rolled) Descale in

HF	Fe	Temp.
90 gpl or higher	10 gpl (max)	78°C

No inhibitor is needed. Although the rate of descaling is slow, substrate loss is considerably lower when compared to HCl/H_2SO_4 pickles.

OR Dip in -

HBF_4	130 gpl	Temp. ≥80°C	nontempered steel

OR

HBF_4	65 gpl	Temp	65°C - tempered steel

The substrate attack is far less compared to HCl/H_2SO_4

TABLE 3

FORMULATIONS FOR CHEMICAL POLISHING AND BRIGHTENING

The treatment is a dip process.

ALUMINIUM [10]:

NH_4HF_2	Dextrin	HNO_3	$Pb(NO_3)_3$	Water	Temp.
80-200gms	10 gms	110-210 gms	0.4 gms	to 1 l	50-60

Only gentle agitation of job is carried out. The operating temp. for the hitherto used H_3PO_4 - H_2SO_4 solution is 100°C.

MAGNESIUM ALLOYS

$Na_4P_2O_7$	Borax	NaF	Water	Temp.
30 gms	67 gms	8 gms	to 1 l	77 - 82°C

followed by immersion in

$NaHF_2$	$Na_2Cr_2O_7 \cdot 2H_2O$	$Al_2(SO_4)_3 \cdot 14H_2O$	HNO_3 (conc)	Water to
15 gms	180 gms	10 gms	125 ml	1 litre

followed by a dip in

NaOH 50 - 100 gpl at RT for 20 sec. for wrought alloys and at 82 - 100°C for castings.

The dichromate pickle may be used for protection of magnisium alloy castings during storage and shipping such as a paint base.

TITANIUM or ZIRCONIUM

NH_4HF_2	HNO_3	H_2SiF_6 (30%)	Water	Temp.
100 g	400-500 ml	200 ml	to 1 l	RT

ZIRCONIUM

NH_4HF_2	H_2SiF_6 (100%)	Zr metal	Water
100 gms	80 gms	3.0 - 4.5 gms	1 l

for alloys low in zirconium

HNO_3(conc)	HF	Glycerine	Temp
450 ml	80 - 100 ml	450 ml	RT

TANTALUM

HAC	H_2SO_4	HF (40%)	Temp.
200 ml	500 ml	100 ml	RT

HNO_3 (conc)	H_2SO_4 (conc)	HF (40%)	Temp.
200 ml	200 ml	100 ml	RT

OR

THORIUM

HNO_3	H_2SiF_6 (30%)	HF (40%)	Temp.
500 ml	20 ml	480 ml	50°C

GERMANIUM

HNO_3 (conc)	HF (48%)	HAc	Bromine	Temp.
500 ml	300 ml	300 ml	10 ml	RT

sufficiently smooth (free from indents, deep scratches, etc) it can be handled straight away. Otherwise, this step is applied to the work after mechanical polishing of the surface. Table 3 gives compositions of chemical polishing/brightening formulations.

A solution [10] consisting of (NH_4HF_2 + $Pb(NO_3)_2$ + dextrin) enables chemical polishing of aluminium at lower temperatures (50-60° C, compared to 100°C hitherto required for H_3PO_4 - H_2SO_4 solution). For magnesium alloys, NaF is the addition agent in a pyrophosphate-borax mixture, followed by a dip in a $NaHF_2$ bearing acid solution. H_2SiF_6 along with NH_4HF_2 is employed for brightening Ti and Zr, while for Th, (H_2SiF_6 + HNO_3) solution does the job. (HNO_3 + HF) solution serves as a chemical polisher for zr and Ta. (HF + glacial acetic acid + HNO_3/H_2SO_4) is used for Ge and Ta.

FOR ELECTROPOLISHING

For materials which cannot be satisfactorily finished by mechanical approaches, or to materials where superior surface finish is desired, this technique is established to confer several benefits. The details are given in Table 4.

High purity aluminium is electropolished in dilute HBF_4 solution or in (H_2SO_4 + HF) solution. For carbon steel, hot solution of HF-water-triethanolamine is used. For electropolishing Ti, Ta and Zr, HF is a constituent of the formulations employed.

IN PREPLATING OPERATIONS

Metal finishers are aware that this stage of metal finishing sequence is crucial in that the adhesion of the electrodeposit, in subsequent operations, depends on this step. One notices from the summary below that in several contexts, fluorine compounds are essential. The detailed bath compositions are given in Table 5.

TABLE 4

ELECTROPOLISHING ELECTROLYTES FOR SELECTED METALS AND ALLOYS

HIGH PURITY ALUMINIUM

BF	Water	Temp.	Cur.Dens. (asf)
25 ml	to 1 l	RT	10 - 20

OR

H_2SO_4 (ml)	HF (ml)	Water	Temp.	C.D.(asf)
10 - 600	2 - 15	to 1 l	60°C	100

CARBON STEEL

HF	Water	Triethanolamine	Temp.	C.D.(asf)
400 g	450 ml	1490 ml	80°C	20 - 200

TITANIUM

Ethlene glycol	HF	NH_4F	NH_4NO_3	Water	Temp.
81-84%	3-4%	5-6%	5-6%	Balance	RT

OR

Ethylene glycol	HF	Water	Temp.	C.D.(asf)
880 ml	60 ml	60 ml	RT	80 - 100

ZIRCONIUM

Glycerol	HF	HNO_3	Voltage
870 ml	43 ml	87 ml	9 - 12 V

TANTALUM

H_2SO_4 (conc)	HF (48%)	Temp	C.D.(asf)
900 ml	100 ml	35 - 45°C	100

HF (48%)	HNO_3	Water	Temp.	C.D.(asf)
100 ml	100 ml	350 ml	35 - 50°C	upto 150

TABLE 5

PREPLATING OPERATIONS IN TYPICAL CASES

Al. Alloys: For casting high in silicon content, after soak cleaning, the material is etched in

HNO_3	HF	Temp.
750 ml	250 ml	RT

prior to immersion zinc formation.

An acid type immersion zinc solution contains

$ZnSO_4$	HF (18%)	Water	Temp.
720 gms	35 ml	to 1 l	RT
	OR		
$Zn(BF_4)_2$	Water	pH	Temp.
75 gms	to 1 l	3.0	RT

For better adhesion in hard chromium plating, prior to immersion zinc film formation, the following pre-etch is recommended

HF	Water	Temp.
50 ml	950 ml	RT

Where immersion nickel is desired on Al castings, dip in

$NiCl_2.6H_2O$	HF	H_3BO_3	Water	Temp.
480 gms	20 gms	38 gms	to 1 l	RT

Zinc Base Alloys: Activating dip, after electrocleaning contains

HF	Water	Temp.
5 - 10 ml	to 1 l	RT

Mg Alloys: Prior to plating and cleaning, the activator carries

H_3PO_4 (con)	NH_4HF_2	Water	Temp.
200 ml	100 gms	800 ml	RT

While alkaline activator consists of

$Na_4P_2O_7$	Borax	NaF	Water	Temp.
40 gms	70 gms	20 gms	to 1 litre	77°C

Table 5 continued

Stainless Steel: Anodically in

$NiCl_2.6H_2O$	NaF	HCl	Water	Temp.	C.D. (asf)	Duration
240 gms	10 gms	60 ml	to 1 l	RT	140	5 mins

Best procedure [11] for activation of stainless steel for chromium plating consists in anodic treatment in

H_2SO_4	HF	Water	Temp.	C.D. (asf)	Duration
650 ml	50 ml	to 1 l	21°C	280	1 min

This is suitable for types 304, 316, super alloy U-700.

Lead and Lead alloys: To ensure good bending on stereo types (Pb-Sn-Sb alloy), leaded brass and soldered parts, prior to plating, dip in -

HBF_4 (42%)	Water	Temp.
250 ml	750 ml	RT

For Leaded bronze surface, employ -

HBF_4 (42%)	Water	Temp.
500 ml	500 ml	RT

For leaded and soldered assembled components with brass, nickel silver like substrate, anodically employ -

HBF_4 (42%)	Water	Temp.	C.D.(asf)	Duration
250 ml	750 ml	RT	15	10 secs (max)

Titanium: For copper plating, activation of the surface is done anodically in -

Ethylene glycol	HF (100%)	Water	Temp.	C.D. (asf)	Time min.
790 gms	150 gms	60 gms	55-60°C	50	15-30

For Chromium plating on Cr-Al containing titanium alloy, for activation, immerse in -

$Na_2Cr_2O_7\ 2H_2O$	HF (48%)	Water	Temp.
400 gms	25 ml	to 1 l	100°C

Table 5 continued

Zirconium: As a preplating step, treat chemically in -

NH_4F	HF (100%)	Water(pure)	Temp.	Duration
35 gms	30 gsm	to 1 l	40°C	1-3 mins

OR dip in

NH_4HF_2	H_2SO_4	Water	Temp.
15 gms	0.5 ml	1 l	RT

Niobium: For plating, activate in - HF (48%) solution at RT with Ac at 200 asf for 1-3 mins followed by desmutting in -

HF (40%)	HNO_3 (conc)	Water	Temp	Time
10 ml	500 ml	to 1 l	RT	15 - 30

Tungsten: Activation prior to plating consists of dipping in -

HF	HNO_3	(H_2O)	Temp.	Duration
300 ml	400 ml	400 ml	50°C	5 mins

Beryllium: For plating, one approach is to form immersion zinc deposit by dipping the clean job in a solution made of -

$ZnSO_4$	$Na_4P_2O_7$	NaF	K_2CO_3	Water
40 gms	120 gms	8 gms	5 gms	to 1 l

at pH 7.5 - 8 and 82° for 5 min.

For nickel plating, for joining purpose, etch in

HNO_3	HF	Water	Temp.
200 ml	100 ml	200 ml	RT

and follow it by immersion zinc formation in -

ZnO	KF	H_2SO_4	Water	Temp.	Time
30 gms	15 gms	25 ml	to 1 l	RT	10 min

Silicon: For plating, activation is carried out in two stages: initial etch in -

HNO_3 (conc)	HF	Water	Temp.	Time
440 ml	180 ml	380 ml	RT	2-3 mins

Table 5 continued

is followed by a dip in 48%HF at RT for 10 sec

Specifically to plate Ni, the clean work is dipped in following solution of pH 1-3 at 50-60 C for 1 mt

HF 70%	Citric	NiCO basic	Sodium Lauryl Sulphate	Water
60 ml	30 g	120 g	1 g	to 1 l

followed by water wash and nickel plating.

Plastics: One of the approaches to prepare ABS and polypropylene for providing bonding to the deposited metal is to condition the surface by dipping in the following solution for 1-5 mins

CrO_3	H_2SO_4	HF	Water	Temp.
50 g	100 ml	100 ml	to 1 l	RT - 35°C

A pre-etch for aluminium castings high in silicon, contains HNO_3-HF, while such an etch in the sequence for hard chrome plating is a dilute HF Solution. Normally immersion zinc is formed out of alkaline baths on aluminium alloys. An acid type is also reported, carrying $ZnSO_4$-HF or $Zn(BF_4)_2$ Again, immersion nickel coating on aluminium castings from $NiCl_2$-HF-H_3BO_3 mixture is recommended in place of zinc plating.

For zinc base alloys, activation is done by dipping in 5-10 ml/1 of HF. The activators for magnesium alloys can be acidic solution with (H_3PO_4 + NH_4HF_2) or alkaline one with ($Na_4P_2O_7$ + borax + NaF).

For adhesion of deposit on stainless steel, anodic treatment in ($NiCl_2$ + NaF + HCl) solution or (H_2SO_4 + HF) solution [11] is suggested. Such an activation is dip process in (HNO_3 + HF) solution for W, Be and Si. Similarly immersion in ($Na_2Cr_2O_7$ + HF) or (NH_4F + HF/NH_4HF_2 + H_2SO_4) solution is carried out for plating on Ti and Zr respectively. In yet another method, anodic treatment in (ethyleneglycol + HF) solution is recommended for Ti, while activation anodically in HF solution with AC is needed for Nb.

Lead and lead alloys need HBF_4 solution for chemical or electrochemical activation.

One approach to ABS and polypropylene for providing bonding of the (electrodeposited) metal is to condition the plastic surface, by dipping in (CrO_3 + H_2SO_4 + HF) solution.

IN ELECTROPLATING

Fluoborate baths are widely used for plating a number of metals like lead, tin, copper, nickel, cadmium, zinc, indium, cobalt [12], iron [13] and alloys like lead-tin, lead-tin-copper [14], cadmium-tin, cobalt-manganese [15] and nickel-cobalt [16]. A few of them are used for barrel plating and for heavy deposition as well. For high speed plating of copper, lead, tin and cadmium, fluoborate baths are utilised, [17]. For electro-tinning fluoborate bath is used [18]. The advantages of fluoborate baths are: nearly 100% anode and cathode efficiencies; smooth and fine grained deposits; high conductivity; high deposition rate; good covering power; ease of preparation of solutions; simplicity and stability of the baths. From hydrogen embrittlement point of view, zinc/cadmium fluoborate electrolytes confer insignificant embrittlement to the substrate.

To a limited extent, silicofluorode baths are used for electrodeposition purposes such as for lead [19], cobalt [20] and cadmium-lead [21].

Baths for continous plating of strips or wires rely on use of fluoride as an important bath constituent. For example, halogen bath for tin carries NaF and KHF_2 or KF [22-25]; and acid zinc bath [26] consists of either NH_4F or NH_4HF_2 Some of these baths yield bright deposits. A couple of alloy baths do use fluoride as an essential chemical in the electrolyte, for example, tin-nickel bath has NH_4HF_2 [27-30], where fluorine content control is important and its presence is absolutely necessary for alloy deposition to take place. Yet another bath has NH_4F and/or NaF [31]. Iron-chromium-nickel bath contains NaF. Complex fluoride salts have been used to obtain smooth and bright deposits as in copper and nickel trifluoro-acetate baths [32].

DEVELOPMENTS IN CHROMIUM ELECTRODEPOSITION

With the introduction of fluorine compounds, the developments in chrome plating have been rapid and their utilization in industry has enormously increased. Fluorine compounds such as HF, $Na/K/NH_4F$, HBF_4, H_2SiF_6, silicofluorides and CrF_3, either by themselves or usually in conjuction with sulphate, have served as catalysts [33-36]. They have enabled brighter deposits in the 'as plated' condition over a wide current density range, a better looking and harder deposit and baths with higher cathode efficiency, better covering and throwing powers and with capacity of withstand current interruptions. The last property means less rejects in production and scope for using such baths for barrel plating. We have baths based on pure chromic acid and on tetrachromate [37] to meet decorative and hard chrome needs. In the latter baths, fluoride addition enabled production of bright deposits [38], which are otherwise dull in the as plated' state.

The concept of self-regulation rendered possible with sparingly soluble compounds like (K_2SiF_6 + $SrSO_4$) [39,40] or (CaF_2 + $SrSO_4$) [41], has eliminated the problem of control of critical concentration of these catalysts. We have a number of baths of the self-regulating type to cater to different needs of platers. Some of them enable deposition of microcracked chromium [42], (which confers higher corrosion resistance to the decorative system) as compared to the one with conventional chromium. Use of CaF_2 and $NaAlF_6$ [43] in chrome baths has reduced the tendency of the bath to etch at low current density areas of the job. In spite of the benefits provided by the fluoride to chrome solution, from the hydrogen embrittlement angle, its behaviour is similar to sulphate.

Barrel chromium deposition relies on fluoride or silicofluoride as catalysts. Black chromium, which is the best selective coating for solar energy applications is successfully plated from baths with fluoride/silicofluoride as catalysts and we have even a self-regulating bath operable at the ambient temperature [44]. Developments in low chromic acid baths - with a view to minimise effluent handling- employ silicofluoride compounds [45].

FOR STRIPPING OF DEPOSITS

Practically useful strippers for reclaiming the defectively plated substrate use fluorine compounds in certain formulations. Some typical formulations are given in Table 6.

An established pratice to strip nickel from steel is to immerse the job in concentrated HNO_3 The stripping rate is rather low in this. Addition of 4 gpl of NaF hastens the stripping by 50-100 fold and it further enables identifying the completion of the stripping process by the cessation of gassing [46]. Nickel on magnesium alloys and anodic coating on aluminium are stripped in (HF + HNO_3) solution by immersion while anodic treatment in (HF + H_2O_2) is reported (47) for tin on lead frames (used in semiconductor work) and in (CrO_3 + H_2SiF_6) for brass on steel.

TABLE 6

STRIPPER SOLUTIONS

Nickel/Steel: Dip in -

HNO_3 (conc)	NaF	Temp.
1 l	4 gms	RT

Nickel/Magnesium: Immerse in -

HF	HNO_3	Temp.
300 ml	150 ml	RT

Tin/Lead frames: Anodically in -

HF	H_2O_2	Additive
30%	40 %	as recommended

Brass on steel: Anodically in -

CrO_3	H_2SiF_6	Temp.
130 gpl	7 gpl	RT

Anodic coating on **Aluminium:** Immerse in -

HNO_3	HF
750 ml	250 ml

FOR QUALITY CONTROL

In analytical work, fluorine compounds have their role, although limited. For volumetric analysis of chromic acid in chrome baths, particularly old baths, fluoride/bifluoride is added to prevent iron interference in the estimation by iodometry. Similarly it is used in the estimation of copper in brass/bronze bath. To keep back the unprecipitated tin, KF is used in the analysis of zinc in tin-zinc bath of cyanide-stannate type.

For testing local thickness of deposits, coulometric method [48] is a reliable method. Fluoride bearing electrolytes find use for checking thickness of certain type of deposits. A few examples are:

Copper deposit on Zinc - H_2SiF_6 (30% w/w) 100 ml + 5 gms. of MgSiF
Silver deposit on copper - KF 100 gpl
Tin deposit on aluminium - H_2SO_4 50 ml/l. + KF 5 gpl
Silver deposit on brass - NH_4 F 50 gpl + Wetting agent 1 gpl.

AS A SPRAY SUPPRESSANT

An important problem faced in chromium deposition from chromic acid solutions is the emission of toxic acid spray thrown out into the shop. This is a health hazard and interfers with the working of the operators, besides corroding the equipment and machinery heavily. Loss of chromic acid due to spray is estimated to be 20-25% of the originally added chromic acid. Present pollution control regulations require that the maximum permissible concentration in the work place be 0.01 mg/m^3 To meet this stringent stipulation, good ventilation and costly exhaust system have to be installed. Use of polypropylene spheres or polystyrene rods/tubes can minimise the problem, but still exhaust arrangement are needed. An alternate answer is to use wetting agents which lower the surface tension of the chrome bath thereby reducing the spray and fumes thrown out and also prevent them from leaving the bath by forming a foam blanket.

Chromic acid being a powerful oxidant and the wetting agents being organic compounds, there has been a problem in identifying chemicals resistant to the hot chromic acid solutions. Developements in complex organic fluorine chemistry have given an answer to this serious problem in the chrome shop. Today we have perfluorosulphonates meeting the requirements. Typical compound is: tetraethyl ammonium perfluoro octane sulphonate [49]. It can be used in pickling solutions to create a better working surroundings.

MISCELLANEOUS

Though of limited application, immersion deposition is commercially practised. For immersion plating of copper/cadmium on aluminium, 48% HF is used together with the corresponding sulphates. For zinc on magnesium, ($ZnSO_4$ + $Na_4P_2O_7$ + NaF + Na_2CO_3) solution is used. To strike copper on this zinc coating, the cyanide copper bath carries KF as an important constituent. To nickel plate directly over this zinc layer, a bath containing 70% HF + citric acid + basic nickel carbonate + sodium lauryl sulphate is employed. Detailed baths compositions are given in Table 7.

Magnesium alloys occupy an important place in fabrication work primarily in aerospace applications. It is chemically and electro-chemically treated to enhance its decorative look,

TABLE 7

IMMERSION DEPOSITION SOLUTIONS

For **Copper** on **Aluminium:**

$CuSO_4$ $5H_2O$	HF(48%)	Water	Temp.
200 gms	10 ml	to 1 l	RT

For **Cadmium** and **Aluminium:**

$CdSO_4$	HF (48%)	Water	Temp.
4 gms	110 ml	to 1 litre	RT

For **Zinc** on **Mg alloys:** at 80° dip in 1 l solution made from

$ZnSO_4$ $7H_2O$	$Na_4P_2O_7$	NaF	Na_2CO_3
50 gms	120 gms	5 gms	5 gms

For **Copper plating** over immersion zinc layer on Mg alloys:

CuCN	KCN	KF	Water	C.D. (asf)
41 gms	68 gms	30 gms	to 1 l	5-10 for 2 min & 20 upto 15 mins (max)

For Nickel Plating over immersion zinc on Mg alloys

HF (70%)	60 ml
Citric acid	30 gm
Basic $NiCO_3$	120 gm
Sodium lauryl sulphate	1 gm
Water	to 1 litre
pH	1-3
Temperature	50 - 60° C
C.D (asf)	30 - 100

corrosion resistance and gnerally to serve as a paint base. Many of these treatments require fluorine compounds. For wrought alloys, pickling in a bifluoride or 60% HF solution followed by boiling for 30 mins. in $Na_2Cr_2O_7$ + Ca/MgF enhances the corrosion resistance and acts as a base for painting. For similar paint needs, all aloys are anodically treated in (NH_4HF_2 + $Na_2Cr_2O_7$ + H_3PO_4) solution followed by sealing in sodium tetrasilicate solution at 95-100° C for 15 mins. For a good shelf life and as a clean up operation, dipping in (CrO_3 + $Fe(NO_3)_3$ + KF) is employed. If one starts with a clear surface, brightening is possible in this solution, in proportion to the fluoride content and the treatment duration. For protection during storage and shipping and as a paint base, castings are immersed in ($NaHF_2$ + $Na_2Cr_2O_7$ + $Al_2(SO_4)_3$ + HNO_3) solution.

TABLE 8

CHEMICAL AND ELECTROCHEMICAL TREATMENTS FOR MAGNESIUM ALLOYS

As a paint base and for corrosion resistance to wrought alloys, treat in -

$Na/K/NH_4HF_2$	HF (60%)	Temp.	Time
50 gpl	187 ml/l	RT	30 secs - 5 mins

followed by boiling for 30 mins. in -

$Na_2Cr_2O_7$. $2H_2O$	Ca/MgF_2
120 - 180 gpl	2 gpl

For a dark brown to black coating as a paint base and for protection to all Mg alloys, treat in -

$Na/K/NH_4HF_2$	Temp	Time
50 gpl	RT	5 mins

followed by dipping in

$(NH_4)_2SO_4$	$Na_2Cr_2O_7$ $2H_2O$	NH_4OH	Temp.	Time
30 gpl	30 gpl	2.5 ml/l	50-60° C	10-30 min

Couple the job and the steel tank for galvanic action

As a paint base - for all alloys - anodically treat in

NH_4HF_2	$Na_2Cr_2O_7$ $2H_2O$	H_3PO_4 (conc)	Temp.	Voltage	Time
360 gpl	100 gpl	90 ml/l	71-82°	40-95 V	2.5-5 min

followed by sealing in 50 gpl sodium silicate solution at 95 - 100° C for 15 mins.

For high corrosion resistance and very high abrasion resistance, anodically treat in -

KOH	165 gpl
$Al(OH)_3$	34 gpl
KF	34 gpl
Na_4PO_3 $12H_2O$	34 gpl
$KMnO_4$	19 gpl
Temperature	RT
Voltage	AC 85 V
C.D.(asf)	18-20
Duration	60-75 mins

Table 8 continued

followed by a dip in -

NH_4HF_2	$Na_2Cr_2O_7$ 2 H_2O	Temp.	Duration
100 gpl	20 gpl	RT	1 - 2 mins

and rinsing in cold and hot water

For good corrosion protection from salt spray for Be, treat in the following medium at RT with ultrasonic agitation at 80 K Hz for 5-15 min.

CrO_3	Fluoride	CrO_3/NaF	pH
0.015 M	0.002 M	15/1	1.6 - 2.0

For high corrosion resistance and very high abrasion resistance magnesium alloys are anodically treated in (KOH $Al(OH)_3$ + KF + Na_3PO_4 + $KMnO_4$) solution followed by a dip in (NH_4HF_2 + Na_2 Cr_2 O_7) solution. Some useful formulations are given in Table 8.

Beryllium is given good protection for salt by dipping in (CrO_3 + NaF) solution [50]. A typical electroless nickel bath contains NaF as an addition agent.

Fluorocarbons [51] are mechanically strong, chemically resistant thermoplastic resins with relatively low toxicity and can be used as tank materials, and as a 'stop off' for jigs/racks. They are suitable for all plating baths and cleaners and withstand temperatures upto 57°C. Some of these resins are polytetrafluoroethylene (PTFE), hexafluoropropylene, perfluoroisobutylene, etc. As heat exchangers in electroplating and for coating heating elements (as for example PTFE coated heaters), these fluoroplastics are useful in electrofinishing [52].

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