MINISTRY OF SUPPLY

ARMAMENT RESEARCH DEPARTMENT

Method of Repair of Worn or Overmachined Steel Components by Electrodeposition of Nickel

A.R.D. ELECTRODEPOSITION MEMORANDUM No. 2

PREFACE

The Armament Research Department (formerly the Research Department, Woolwich), has for many years carried out research and development on electrodeposition and electroplating problems for the three Services. Particular attention has been given to the development of methods of repairing worn, corroded or overmachined parts, and of chromium deposition for surface hardening and other special applications. During the war this work has been directed by Mr. A. W. Hothersall and carried out at the Department's laboratories at University College, Swansea.

This report on the "Repair of Worn or Over-machined Steel Components by Electrodeposition of Nickel," has been reproduced as "Electrodeposition Memorandum No. 2," in order that it may obtain a wider circulation.

Additional information on the subject of this memorandum and enquiries on all problems connected with electrodeposition and other coating processes (including electroplating) may be made to the Chief Superintendent of Armament Research at the following address:—C.S.A.R. Liaison Officer, c/o S.T.A.M., Room 1043, Shell Mex House, Strand, London, W.C.2 (Tel.: Gerrard 6933, Ext. 740).

If desired, arrangements can be made for personal consultations with responsible representatives of private contractors (particularly Ministry of Supply contractors) or for visits to works by members of the staff of the Armament Research Department for discussions and investigations of problems arising.

Acknowledgment is made to the Director General of Scientific Research and Development, Ministry of Supply, for permission to publish this Memorandum, previously issued March, 1943, for confidential circulation only.

R. H. GREAVES,
Superintendent of Metallurgical Research.

January, 1944.

Note to Abstractors.—This Memorandum is an official publication and should be indexed under the authorship of the Ministry of Supply (Armament Research Department).

MINISTRY OF SUPPLY

ARMAMENT RESEARCH DEPARTMENT

METHOD OF REPAIR OF WORN OR OVERMACHINED STEEL COMPONENTS BY ELECTRODEPOSITION OF NICKEL*

This report describes in outline a process for the reclamation of worn or overmachined steel components of guns, carriages, etc., by building up with nickel by electrodeposition followed by machining to size. The methods described are the outcome of research and have been established by practical use over a number of years. Application may be made to this department for further information or assistance in case of difficulty.

The essential stages in the process are as follows:—

1. Remove excess of grease, dirt, etc.; wire.
2. Stop-off with wax; fix special anode if necessary (*e.g.*, for building-up inside hole).
3. Clean electrolytically as cathode in alkaline solution; rinse.
4. Etch anodically at high current density in sulphuric acid solution (work passive); rinse.
5. Build up in nickel tank for required time.
6. Rinse, dry, remove wax.
7. Heat treat at low temperature.
8. Remove wire, clean and inspect.

Preparatory Processes

General Note.—Since it is essential that the deposit be strongly adherent to the article, much care must be taken with the preparatory processes on which the adhesion depends. Conscientious attention to these processes is essential to the success of the method.

STAGE 1.—*Initial Cleaning and Wiring*

Excess of grease and dirt can be removed in a vapour degreasing plant or by immersion in a hot metal cleaning solution. If these facilities are not available, the article should be wiped with rags soaked in an organic solvent such as trichlorethylene or petrol. Special care is required to remove grease and solvent from screw threads and hidden cavities, from which it might otherwise exude during nickel deposition. Copper wires of a suitable gauge for carrying the maximum currents used (*e.g.*, in the anodic acid cleaning) are attached by securely twisting them or by soldering; alternatively the article is clamped in a jig.

* A.R.D. Electrodeposition Memorandum No. 2.

STAGE 2.—*Stopping Off*

Composition of Wax.—Stopping off is preferably carried out with a wax coating applied by dipping the article in molten wax described below. The wax mixture should be resistant to the action of the cleaning solutions and the depositing solution, and should not contaminate them. It should be adherent to the metal surfaces and not unduly brittle at low temperatures nor unduly soft at the bath working temperature. It should not fume on melting or decompose when held molten for long periods.

A mixture of amorphous petroleum wax and a hard, high melting point hydrocarbon wax of the paraffin or ceresin type has all the above properties but is in short and fluctuating supply. The position is not at present sufficiently clear for a recommendation.

A mixture used with moderate success is paraffin 90–93, carnauba 10–7 parts; this mixture varies in properties according to the grade of carnauba and it is sometimes necessary to add up to 10 per cent. of beeswax.

If desired, Seekay wax or Halowax may be used for stopping-off in nickel deposition, but these waxes are more expensive and require special tanks fitted with exhaust arrangements to remove fumes; it is also less easy to prevent them from adhering to surfaces upon which deposit is required.

Method of Application.—The wax mixture should be heated in a steel tank to a temperature of about 15–30°C above its melting point, but preferably below 100°C. The surfaces on which deposit is not required are coated with the wax mixture, but it is necessary to protect areas that are subsequently to receive deposit from wax, as traces of this material are liable to result in a non-adherent and in a pitted deposit. For this reason parts of the article upon which wax is not required are covered with a paste of powdered chalk and glycerine, and, while this coating is still wet and the article is warm from the degreasing (or from pre-heating) it is immersed in the molten wax in which it should be allowed to remain for several minutes until it can be removed without immediate setting of the adherent wax film. The article is then lifted out of the wax and allowed to cool until the wax film is tacky, after which it is redipped several times with intermediate cooling until a sufficiently thick wax film has been obtained. As soon as it has become hard, the wax may be cut through with a sharp knife along the edge of the underlying chalk paste, and peeled off the surfaces that have been protected with this mixture. Accidental wax splashes on the depositing surface should be removed by scraping and the scraped areas should then be carefully cleaned with a rag moistened with a suitable solvent such as trichlorethylene or carbon tetrachloride.

Copper connecting wires are difficult to coat satisfactorily with wax and are preferably stopped off by means of thin rubber tubing. Protection of sharp edges and corners from unrequired deposit can be assisted by winding electrician's insulating tape over them prior to waxing. Other devices *e.g.*, painting molten wax on to the article, are necessary in special cases.

STAGE 3.—*Electrolytic Cleaning in Alkali Solution*

The following solution, contained in an iron tank, is suitable:—

Sodium hydroxide (caustic soda) ..	8 oz.
Sodium carbonate (soda ash) ..	8 oz.
Water	1 gallon.

Proprietary metal cleaning solutions may alternatively be used. The solution should not be heated above 40° C. (104° F.) unless high melting point waxes such as Seekay wax have been used for stopping-off. The solution may be used at room temperature for most purposes if desired.

The waxed articles are immersed in the alkali tank and connected to the central negative bar. A current of approximately 50 amperes per sq. ft. of exposed metal surface is passed through the tank for 15–30 minutes, the article being the cathode. The article is then lifted out and closely inspected for traces of wax on the exposed surface. If present, these cause "water break" and are fairly readily seen; they are scraped with a knife and the surface is rubbed over with a moist rag dipped in pumice powder. Further alkali treatment is then given. The current density in this tank is not of critical importance and a number of articles can safely be treated together.

STAGE 4.—*Electrolytic Cleaning in Acid Solution*

(*a*) *Steel Surfaces*

Preferred Method. The solution is prepared by slowly adding sulphuric acid to water, with vigorous stirring, in the proportions 30 H_2SO_4: 70 H_2O by weight or 22 H_2SO_4: 78 H_2O by volume (sp. gr. 1·22 at 15° C.). It is contained in a lead-lined tank fitted with lead cathodes which are "lead burnt" to lead covered brass rods (alternatively the lead lining may be used as cathode). The solution is used at room temperature.

After a thorough washing in clean water, one article or group of articles wired together is placed in the acid cleaning tank and connected to the central electrode bar; the article must be the anode. A double-throw switch is provided to enable the article to be made cathode if required to activate the metal or to dislodge solid residues which have accumulated during anodic treatment. It is of the utmost importance that this switch should be in the correct position.

The current is raised to a value of at least 200–300 amperes per sq. ft. of exposed metal surface and maintained at this value for 8–10 minutes after the commencement of gas evolution. The article is then removed from the tank, quickly examined, rinsed and placed without delay in the appropriate nickel tank. It is very important that the time elapsing between breaking the electrical circuit in the acid tank and connecting the article to the cathode bar in the nickel tank should be as short as possible, preferably not more than 30 seconds. At the same time it is important that the whole of the cleaned steel surface should be closely inspected since a condition leading to defective adhesion may usually be detected and rectified at this stage. The surface should be of uniform silvery grey colour and free from black

particles; if an undue delay has occurred or if the surface appears black, the high current density treatment should be repeated for a short time, using a higher current density if necessary.

Alternative Method.—The following alternative treatment may be used:—

Connect the article as anode in the acid cleaning tank as above but use a current density at first of only 20 amperes per sq. ft. for 10 minutes; then raise the current density to at least 200–300 amperes per sq. ft. and maintain for three minutes observing the directions given above.

This alternative involves less heating of the solution and may be desirable if the atmospheric temperature is high or if the volume of acid solution is restricted.

NOTES ON STAGE 4

(1) It is important that the temperature of the acid solution should not exceed 25° C. as passivity may not readily be obtained above this temperature. If the normal air temperature is likely to exceed 25° C., means of cooling the solution (*e.g.*, by a lead cooling coil) may have to be employed. If difficulty is experienced in working to the above instructions owing to the temperature being too high, the advice of this department should be sought.

(2) With continued use the acid becomes green in colour due to dissolved metals and is less effective. It is cheaper to renew the acid than to attempt to cleanse it but in case of doubt an adhesion test on a scrap part, preferably of an alloy steel, may be carried out. Failure to clean an alloy steel to a silvery grey surface is usually a sign that renewal is necessary.

(*b*) *Nickel Surfaces*

Articles previously built up with nickel should be treated by the method described under "Interruption of Current" (page 7).

This method is essentially the same as that used for steel with the addition of a final "flick" of the reversing switch to make the article momentarily cathodic before removal from the acid cleaning tank.

(*c*) *Cleaning Treatments for Special Steels, Cast-iron or Non-ferrous Alloys**

Enquiry will usually result in information being provided on the type of steel. If the specification is known this will be sufficient. Steels can be broadly classified into plain carbon steels, low alloy structural steels (as generally used for gun barrels, breech mechanism parts and for many carriage and engine parts), stainless and similar high alloy steels and tungsten steels. Good adhesion should be obtained by the recommended method to all but the stainless and tungsten steel classes. It is recommended that these steels, which are in fact rarely offered for repair, should not be treated without further reference to this department.

With plain carbon and low alloy steels, there is generally an increasing difficulty in obtaining sound adhesion with the introduction of alloying metals, and with increase in the carbon content; hard steels

*A separate Memorandum dealing with cleaning treatments for these metals will be issued.

generally give more difficulty than soft steels. Thus, whilst satisfactory results are obtainable if the recommended method is followed, any departure from it is likely to be attended with more serious consequences when alloy or hardened steels are being treated than with mild steel.

Brasses and other copper alloys vary much in composition and it is difficult to suggest a treatment applicable to all. Alloys containing tin, in particular, need special processes, information on which can be obtained on application. Aluminium and zinc base alloys are not generally suitable for the process.

Cast-iron articles may also be treated in the above manner, but the adhesion of the deposit is usually less satisfactory; deposits on white or malleable cast-iron are more adherent than those on cast-iron containing considerable free graphite. If nickel deposits are required on cast-iron parts which are liable to be subjected to severe stresses or to use at high temperatures, the advice of this department should first be sought.

STAGE 5.—*Nickel Deposition*

Choice of Nickel Solution

Two solutions are available for the deposition of heavy nickel coatings for building up undersized components (*see* Table 1). Solution No. 1 produces hard deposits and has better throwing power than solution No. 2 which produces softer deposits. Solution No. 2 can be used at a higher current density than No. 1 and is to be preferred where freedom from pitting is essential; owing to its inferior throwing power, however, the use of a higher current density may not produce a higher rate of deposition in recessed or shielded areas.

For general use in treating miscellaneous components of all descriptions solution No. 1 is preferred. It is advantageous to install both solutions if possible. Solution No. 2 is usually preferable for building up the bores of holes using an internal anode.

TABLE 1.—*Composition of Nickel Solutions and Properties of Deposits*

Compositions.	No. 1 ("Hard") Solution.	No. 2 ("Soft") Solution.
Nickel sulphate (crystals) ..	1 lb.	2½ lb.
Potassium or sodium chloride	1¼ oz.	3⅓ oz.
Ammonium sulphate ..	3⅓ oz.	—
Boric acid (crystals) ..	Nil.	4⅔ oz.
Water (*see* p. 6)	1 gallon	1 gallon
pH value (colorimetric) ..	5·5–5·9 (brom. cresol purple).	3·0–3·5 (brom. phenol blue).
Temperature	37 ± 3° C.	37 ± 3° C.*
Maximum average current density amps/sq. ft.	15	25–30 (greater with agitation).

* Higher temperatures may be used with advantage in speed of deposition if the stopping-off wax is suitably adjusted.

TABLE 1—*contd.*

Compositions.	No. 1 ("Hard") Solution.	No. 2 ("Soft") Solution.
Properties of Deposit—		
Hardness (Brinell hardness range).	300–400	150–250
Wearing properties ..	Good under ordinary lubricated wear. Little difference between hard and soft types. Poor under heavy loading in contact with steel, especially unlubricated, due to tendency to scoring.	
Ductility	Varies from fairly ductile (10–15 per cent. elongation) to moderately brittle.	Ductile, 20–30 per cent. elongation.
Average maximum rate of deposition in. per hour.	·0005	·0005–·0015
† Throwing power	Moderate.	Poor.
Liability to pitting	Moderate.	Slight or Nil.

† Relative rate of deposition on outstanding parts and recesses.

Method of Preparation

Clean water free from appreciable metallic or organic impurities is usually satisfactory for the preparation of nickel solutions. If hard water is used the replacement of evaporation losses may eventually cause calcium sulphate to crystallise out. Soft or distilled water, if available, is therefore preferable.

The solution is prepared by dissolving the salts in warm water. A convenient method is to place the salts in small quantities at a time in the filtering vessel and to circulate the solution by means of the air lift. The solution should be stirred from time to time to prevent local saturation. A freshly prepared solution is frequently contaminated with small quantities of soluble and insoluble impurities. It should therefore be filtered and a test deposit prepared in the solution or in a small portion of it, under the recommended conditions. If this deposit is unsatisfactory the whole solution should be treated with potassium permanganate as described in Appendix II or alternatively it should be electrolysed at a low current density (1–5 amps./sq. ft.) using a cathode of large area until about 5 ampere-hours per gallon have passed. The

"ageing" cathode may be sheet steel or spare nickel anodes may be used as cathodes, if no large amount of foreign metallic impurity is present in the solution; they have the advantage that the deposited nickel may be re-used.

Operation of the Bath

Articles acting as cathodes should be carefully arranged in the bath so that the distribution of the current over the surface is as uniform as is consistent with economical use of space in the tank. Anodes may be adjusted as well as cathodes. Anode connections should be regularly cleaned to avoid "dead" anodes.

The current density during nickel deposition should be regulated as closely as possible to 15 amps./sq. ft. of exposed metal surface in the hard solution. Slightly higher current densities, up to 30 amps./sq. ft. may be used in the soft solution without agitation; with agitation and with increased temperatures considerably higher currents may be possible, especially when treating articles of similar size without sharply contoured surfaces. As far as is possible, articles having greatly differing areas of metal surface exposed should not be treated together in the same tank at the same time.

Estimation of Time of Deposition

Estimation of the time of deposition may be based on an average rate of building up of ·0005 inch per hour when the current density is 15 amps./sq. ft. plus a fixed allowance of 0·01 inch for machining. This calculated time should be ample for most repairs and may be capable of reduction for certain types of repair as a result of experience. A more generous allowance is often necessary where the repair is required in a deep recess or in a sharp corner but such exceptions are difficult to define and can only be judged on the basis of experience.

Interruption of Current

It is important that the depositing current should not be interrupted while deposition is proceeding. Any such stoppage of current, unless of momentary duration, is liable to result in the production of a laminated deposit. In the case of an accidental interruption of current, it is advisable to switch off the depositing current at once and to remove all articles from the nickel tanks, and to treat them as follows:—

(*a*) Rinse and treat as cathode in the alkaline cleaning tank (Stage 3) at about 50 amp./sq. ft. for five minutes.

(*b*) Rinse and treat as anode in the 30 per cent. sulphuric acid solution at a current density of 200 amp./sq. ft. for five minutes.

(*c*) At the conclusion of the high current density treatment, the article is made cathodic for a brief period (not less than one second, not more than 15 seconds) by means of the reversing switch and is then removed from the acid tank, washed and inserted in the nickel tank with the least possible delay.

It is essential to the success of this process that the sulphuric acid solution should be free of impurities such as copper which may be deposited in a non-coherent form during the cathodic treatment. If there is any doubt as to the purity of the sulphuric acid, a test deposit not less than about 0·02 inch thick should be made on steel or nickelled steel using cleaning treatments (*a*) (*b*) and (*c*) ; this deposit should be subjected to bending or chipping tests to determine that the adhesion is satisfactory.

The above treatment should only be applied to articles upon which no nickel has been deposited after the interruption in current. If the current has been restored after an interruption and the articles have not immediately been removed from the bath, no attempt should be made to apply this treatment and the deposits should be stripped.

Deposition on Internal Surfaces

The internal surfaces of shallow holes of reasonably large diameter may be built up in solution No. 1 without the use of internal anodes. For deep holes or for building up the base of a deep recess, internal anodes are usually necessary. Anodes made of nickel wire, rod, or strip may be fixed in position, after stopping off, using jigs of insulating material (*e.g.*, ebonite). Such anodes should be bagged with carefully washed calico. The article, with anode, is then given the usual cleaning treatment, the internal anode being connected to the anode rod by a flexible lead ; it is generally advantageous to insulate it from the cathode rod in the nickel bath (*e.g.*, by wrapping a thick sheet of rubber around the rod), the connection to the cathode rod being made by flexible leads through a portable (sliding) resistance and ammeter. To enable this method to be used to best advantage, it is desirable to connect the main controlling resistance of the nickel bath to the negative lead, the anode rods being connected directly to the positive bus bar.

Nickel Anodes

For building-up with heavy deposits, electrolytic nickel anodes if obtainable are recommended in preference to rolled, cast or depolarised anodes. It is generally advisable to enclose the anodes in bags although, with still solutions which are continuously filtered, bagging is sometimes not essential. Where it can be avoided, the solution is less liable to become contaminated with organic matter. Bags made of woven glass cloth are ideal but expensive.

Treatment After Plating

STAGE 6.—*Dewaxing*

When the calculated time of deposition has passed, the article is withdrawn from the nickel tank and the current re-adjusted. The article is rinsed and examined ; if possible it is measured to determine whether sufficient deposit has been applied. If not or if further deposition seems necessary the article may be treated as described under " Interruption of Current," and replaced in the bath. If the deposit is satisfactory the article is de-waxed, a convenient method being to hang it in the molten wax for a few minutes, then remove and drain.

STAGE 7.—*Heat Treatment*

After de-waxing, the article is heat treated for two hours at 150–200° C. This may be conveniently done by immersion in a steel tank containing oil of high flash point, *e.g.*, Belmont oil (Price & Co.) or seal oil.

Low temperature heat treatment of deposits is an important part of the process and should not be omitted. It expels absorbed hydrogen, thus removing hydrogen embrittlement and improving adhesion. A temperature below 150° C. (300° F.) is only partially effective and therefore this temperature is to be regarded as a minimum. The upper limit of temperature is that likely to cause injury to the component either by " drawing the temper " or by scaling. Except for specially hardened components, therefore, a temperature up to 250° C. can normally be used with safety and advantage.

STAGE 8.—*Inspection* *

It is essential that the outgoing work be very carefully inspected both as a check on the process and to avoid the serious distrust of the process which arises from a small number of failures. Certain simple control tests should also be performed at regular intervals. Notes on these points are given below.

Adhesion.—All deposits should be examined for obvious lifting, exfoliation or cracking. In cases of doubt the hollow sound emitted when a deposit which has lifted is tapped with a hammer is a useful test. This test does not, however, indicate a deposit which is non-adherent but which lies closely to the steel. Attack at an edge or corner with a hammer and chisel is a reliable and stringent although a somewhat destructive test, unless performed with care. This test is best carried out on a scrap piece of alloy steel processed for the purpose. Deposits should be examined for adhesion after heat treatment which assists in loosening non-adherent coatings by differential heat expansion.

Defects of the Deposit and Unsuitable Mechanical Properties

Examination of the deposit for surface appearance and defects before heat treatment or machining often yields valuable information on the chemical condition of the depositing solution. Unduly bright deposits and cracks are signs of unsatisfactory mechanical properties and such deposits should not be issued. Nodules and growths are usually present to some extent but certain forms are very undesirable as they are knocked out in machining leaving a pit or hole. Dark and burnt deposits are frequently unsound even if the surface appears compact. The cause and remedy of most of these defects is given in Appendix II.

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*A separate Memorandum on Inspection will be issued.

APPENDIX I

Control of Plant and Solutions

I.—*Plant*

Current Supply.—It is imperative that the depositing current should not be interrupted or be unduly raised or lowered. Special precautions should be taken to prevent stoppage of the current supply by accidental disconnection of the circuit or failure of the generator. A simple indicator consisting of an electro-magnet connected across the deposition circuit can be arranged to show, by the falling of an armature, any cessation of the current.

A convenient method of protection against failure of the current supply is the provision of a battery of three or four accumulator cells of high discharge rate which are automatically switched into circuit on failure of the normal supply ; manual switching has the disadvantage that it can seldom be operated within the requisite time and should not be used. This precaution is specially advised where deposition current is drawn from rectifiers when temporary stoppage of the electrical supply might pass unnoticed.

Cleaning and depositing currents should not if possible be taken from a common source but, where this is unavoidable, care should be taken that changes in voltage caused by switching heavy cleaning currents on or off do not cause excessive changes in the depositing current.

A battery current supply has the additional advantages that it can be used for depositing current when cleaning is in progress and at times of light load or whilst the generator is being cleaned or overhauled.

Cleanliness of Tank Electrode Bars.—The cathode bars of the nickel depositing tanks must be kept in a clean state. Similarly anode bars, anode hooks and other parallel contacts in the depositing circuit should be regularly inspected and cleaned so that unnecessary resistance is eliminated. The anode bar of the acid cleaning tank should also be kept clean to prevent fluctuation of current density in this critical cleaning stage and undue heating of the contact by the relatively heavy currents used. In the cleaning of these bars and hooks, especial care should be taken that the corrosion products, particularly those of brass or copper, are not allowed to fall into the solutions.

Ammeters and Voltmeters should be checked at intervals to detect gross inaccuracy.

II.—*Solutions*

The chemical control of the process is not difficult or elaborate and frequent analyses are not necessary. The type of control needed is summarised in Table 2 (page 13) and described in more detail below.

The alkaline cleaning bath should be renewed when it becomes obviously dirty or ineffective. Regular skimming of the surface is recommended. Analysis is not necessary.

The sulphuric acid solution can be checked at intervals (*e.g.*, weekly) with a hydrometer ; it should have a specific gravity between 1·20 and 1·25. In warm weather or when correct cleaning becomes difficult the temperature may be too high. This is readily checked with a thermometer. It should not exceed 25° C. (77° F.).

The nickel solution should be tested at frequent intervals for temperature, pH value and specific gravity. The pH should be measured daily. It will be found in general that it tends to rise and sulphuric acid needs to be added to correct this ; a guide to the amount required is given in Table 3. If the opposite tendency is noticed it is usually an indication of a defect which should be promptly investigated and remedied ; the tank lining or a pipe or fitting may be acting as a secondary electrode for example. Increase in pH value may be effected by stirring in powdered or " plastic " nickel carbonate, with subsequent filtration if necessary.

The normal rise in pH during working implies an increase in the nickel sulphate content of the solution relative to the other constituents. All constituents of the bath are removed equally by drag out. Both these effects are, however, small and provided that the density of the solution is checked and corrected at intervals no frequent analysis is essential. Estimation of nickel, chloride and ammonium may be carried out at long intervals, say annually, or at six-monthly intervals. It is wise to record all additions to the nickel solution other than water.

When the deposit is defective and the operating conditions, after careful checking, are found to be correct, contamination may be suspected. The permanganate test for organic matter, described in Appendix II, page 19, may be tried and also qualitative analytical tests for foreign metals. It is convenient from time to time to make test deposits under standard conditions for examination of hardness, ductility and appearance (texture and presence of defects), *see* page 19. Deposits from uncontaminated solutions should have the properties indicated in Table 1, page 6 ; they should be matt in texture and should be substantially free from pits with solution 1 and entirely free from pits with solution 2.

TABLE 3.—*Millilitres of Concentrated Sulphuric Acid to Restore pH to Lower Value of Working Range*
(*Colorimetric pH Values, not Corrected*)

pH Value.	No. 1 "Hard" Solution. Working Range pH 5·5–5·9 Volume of Acid Mls. for 100 Gallons of Solution.	pH Value.	No. 2 "Soft" Solution. Working Range pH 3·0–3·5 Volume of Acid Mls. for 100 Gallons of Solution.
5·5	0	3·0	0
5·7	18	3·2	12
5·8	24	3·4	24
5·9	36	3·6	36
6·0	48	3·8	48
6·1	84	4·0	60
6·2	114	4·6	66
6·3	144	5·0	96
6·4	192	5·2	108
6·5	252	5·4	132
6·6	312	5·6	180
6·7	396	6·0	264
6·8	480	6·3	408
6·9	588		
7·0	720		

Filtration of Solution

Nickel solutions used for building-up should preferably be filtered continuously. A simple method is to fit an air lift which pumps the solution from the bottom of the tank into a filtering vessel from which it flows back into the top of the tank by gravity. Felt filtering bags are preferably avoided; they may be replaced by a lead vessel with a perforated bottom, the filtering bed consisting of a layer of glass wool, two inches in thickness, covered with a layer of "filter aid" or kieselguhr; a perforated lead plate is placed over the layer of kieselguhr to prevent its disturbance by the stream of solution.

TABLE 2.—*Control of Solutions*

	Gravity.	Working Temperature.	pH.	Analysis.	Behaviour in Operation.	Attention or Treatment.
Alkaline bath	—	Room.	—	—	Formation of scum	Periodic removal of scum. Change solutions at intervals and when obviously dirty or inefficient.
Sulphuric acid bath.	Weekly.	Not to exceed 25° C.	—	—	Changes slowly to green colour due to dissolved metals.	An alloy steel specimen should be cleaned to a silvery grey surface. In cases of doubt, an adhesion test on an alloy should be made, and if the adhesion is unsatisfactory the acid should be replaced. A pronounced green colour, indicating contamination of the solution with dissolved metals is an indication that the solution should be discarded.
Nickel solution.	Weekly.	Daily.	Daily.	Annual estimation of (*a*) in hard solution nickel, chloride, ammonium. (*b*) in soft solution nickel, chloride, boric acid, alkali metals.	Tendency to be contaminated from (*a*) organic, and (*b*) metallic impurity.	(*a*) treatment with permanganate. *See* Appendix II. (*b*) *See* Appendix II.

APPENDIX II

Avoidance of Defects

Unsatisfactory repairs may usually be classified under one of the following headings :—

(1) The deposit fails to adhere to the steel.
(2) The deposit is laminated.
(3) The deposit has unsatisfactory mechanical properties, *e.g.*, it is too hard or too brittle.
(4) The deposit has local defects, *e.g.*, pits or growths.
(5) The deposit although sound and adherent is insufficient in thickness.

Failures of classes 1 and 2 are often not detected until much of the final machining has been done and thus cause much loss of labour. In such a case it is very desirable to inspect the article to determine if possible the cause of failure. A classification into type 1 or 2 will usually be easy.

Failures in class 1 may be due to (*a*) failure to carry out the recommended process ; (*b*) the grade of steel (*see* page 4) ; (*c*) too high an initial current density in the nickel bath. (*a*) is the most common cause of failure and is usually due either to incorrect control of the current during anodic cleaning in sulphuric acid or to the use of a contaminated sulphuric acid solution. In particular, the instructions for control of high current density etching should be carefully observed and, as noted above, it is advisable to renew the acid solution at intervals.

Failures in class 2 are almost always due to interruption of the depositing current either locally, for example, by disconnection of the article from the cathode bar, or by general failure of the supply ; excessive current density for a short period (burning) is sometimes responsible. If failures in this class occur the electrical arrangements should be reviewed.

Failures in classes 3 and 4 are usually due to a defective condition of the solution (except that pits are sometimes due to improper cleaning, for example, contamination of the surface with wax, or to leakage of grease or oil from crevices in built up constructions) ; remedial measures are indicated below.

Failures due to class 5 are usually due to lack of appreciation of the non-uniformity of deposition on irregular articles and are usually recoverable, although at considerable trouble ; for example the removal of grease and oil from the " scant " area (*i.e.*, the portion of the deposit not touched by the tool in machining) is sometimes difficult and requires special care.

The types of failure and remedies are summarised in Table 4 (pages 16, 17 and 18).

Contamination of the Solution

Contamination of the solution is indicated by an excessively hard, brittle, lustrous or pitted deposit; by exfoliation; by dark coloured or green streaks on the deposit; or by excessive gassing and frothing. A number of possible defects, together with their probable cause and treatment, are set out in Table 4. The following workshop tests are given in addition :—

Copper.—Examine anodes for a coppery film especially when bath has not been used for a few hours, or insert a freshly abraded piece of steel in the solution for a few minutes and examine for copper deposit.

Chromium.—A test within the capability of a work's laboratory is given below :—

(*a*) Chromium present as chromic acid or dichromate. Acidify a sample of solution with dilute sulphuric acid and add a small quantity of an acetic acid solution of diphenyl carbazide. A purple or red colour indicates hexavalent chromium.

(*b*) Chromium present in the trivalent form. Excess of sodium hydroxide is added to a sample of solution and a small quantity of sodium or hydrogen peroxide. The solution is boiled, cooled, acidified with dilute sulphuric acid and tested as above.

Iron.—Usually present in all solutions especially those operated at low pH values. Add ammonia to a sample. A *large* amount of brown flocculent precipitate indicates a deleterious amount of iron.

If appreciable amounts of these metallic impurities are found in the solution, attempts should be made to discover the cause and to apply a suitable remedy.

Metal articles dropped into the solution should be recovered at once ; metal electrode bars should be kept clean, but should not be cleaned over the solution. Floating scum and debris, should be skimmed from the solution and crystallised salts washed down from the sides of the tanks and tops of the anodes.

Aqueous extracts of soft woods, textiles, etc., are particularly detrimental and contact of the solution with organic materials of this kind should be avoided. The enclosure of the anodes in bags prevents finely divided conducting particles passing into the solution and causing growths on the cathode ; their use is essential if the solution is vigorously agitated. Anode bags should be prepared from cloth pre-treated to remove dressing or from fabric made from glass wool. Covers for the tanks should be impervious to condensed moisture. It is advantageous to maintain deposition at a small current during idle periods ; this may be economically arranged by hanging an anode on the cathode bar. A contaminated solution can frequently be improved by electrolysis at a low current density (1–5 amp./sq. ft.) on a cathode of large area ; alternatively, where the contamination is due to organic matter, the solution may be treated with potassium permanganate as described below.

TABLE 4.—*Cause and Treatment of Various Defects of Nickel Deposits*

No.	Defect.	Causes.	Remarks.	Action.
1.	The deposit fails to adhere to the steel.	(*a*) Incorrect cleaning procedure.	Insufficient degreasing. Incorrect control of current during acid etching. Incorrect concentration of acid. Contamination of acid. Delay in transfer.	Refer to instructions and correct.
		(*b*) Grade of steel.	Check composition of steel. High chromium (stainless) steel, tungsten steel, cast-iron should not be treated.	Apply for special method of treatment.
		(*c*) Initial plating current too high.	Unsuitable current control or measurement, or deposition on very large and very small articles in the same bath.	Measure area and calculate initial current on basis of 5 amps./sq. ft.
2.	The deposit is laminated.	(*a*) Interruption of the depositing current.	General failure of current supply. Local failure by disconnection of the article from the cathode bar.	Provide stand-by current from accumulators with automatic change-over. Check over and clean all connections. Inspect electrical apparatus.
		(*b*) Short periods of excessive current.	Often caused by removal of other articles without readjustment of current or by inadvertent rise in supply voltage.	Inspect current at frequent intervals.
3.	The deposit is too hard or too brittle.	(*a*) Defective condition of solution.	Contamination by organic materials (wood, textiles, wax oil). Contamination by inorganic materials (nitric or chromic acid, copper, zinc, iron).	Search for and remove source. Treat solution with permanganate (Appendix II). Remove dissolved metallic impurity.
		(*b*) Defective conditions of operation.	pH value too high. Temperature too low. Current density excessive.	Check and correct.
4.	Local defects.	(*a*) Pitting.	Organic contamination. Unsuitable pH value. Ineffective degreasing.	*See* 3(*a*) above. Do not add hydrogen peroxide.
		(*b*) General small scale roughness.	Suspended conducting particles in solution.	Filter solution. Bag anodes Avoid agitation.
		(*c*) Large and excessive growths especially on edges and corners.	Irregular and excessive current distribution.	Improve current distribution by suitable grouping of articles, fitting of shields of rubber and adjustment of stopped-off areas.
		(*d*) Bush-like black growths.	Usually due to contamination by copper or cadmium.	Examine anodes for copper film. Electrolyse solution at a low current density on a scrap cathode.
		(*e*) Dark coloured or black streaks and growths.	Usually due to contamination by zinc, cadmium or copper.	Examine anodes for copper film. Electrolyse solution at a low current density on a scrap cathode. Search for and remove cause.

TABLE 4.—*Cause and Treatment of Various Defects of Nickel Deposits—(continued)*

No.	Defect.	Causes.	Remarks.	Action.
4.	Local defect—*contd.*	(*f*) Green or dark coloured slime on high current density areas (burning).	Excessive current density. Contamination of solution by chromium compounds.	Inspect electrical connections and meters. Recalculate areas. Electrolyse solution at a low current density on a scrap cathode.
5.	Insufficient thickness of nickel deposit.	Incorrect calculation of area. Inadequate allowance for non-uniformity of deposition on irregular articles and for increase of area due to growths on edges, wires, etc.	Treatment together of articles of widely different exposed area, leading to insufficient deposit on the larger areas.	Check meters. Check areas. Arrange articles and anodes and change stopped-off areas to improve uniformity of distribution. For thick deposits, current should be increased as deposit increases in area. Use auxiliary anodes or shields if possible. Treat articles of widely different exposed areas separately.

Chromic acid is very deleterious in nickel solutions ; in fairly small concentration it may prevent nickel deposition altogether or may so reduce cathode efficiency that excessive gassing occurs during deposition and the thickness of deposit obtained is less than that calculated. Nickel deposition should not be carried out in close proximity to chromium deposition and as far as possible separate cleaning solutions, jigs and stopping-off waxes should be used for the two processes. If nickel solutions become seriously contaminated with chromic acid, it is generally best to discard them. Slight contamination may be rectified by electrolysis using a scrap cathode and a low current density.

The most effective method of determining the behaviour of the bath is regularly to prepare, *e.g.*, monthly, a deposit ·005–·01 inch thick on a stainless steel or aluminium sheet on which the deposit will be non-adherent ; alternatively a copper or brass cathode suitably treated to make the deposit non-adherent may be used. If the deposit curls off the cathode during deposition or is excessively brittle when detached, an incorrect pH value or the presence of impurities is to be suspected. If the deposit is sound, a standard bending test, *e.g.*, around a rod one-eighth inch in diameter, may serve to reveal variation in its properties. It is important to standardise the thickness of deposit in any form of bending test.

Occasional treatment with permanganate followed by thorough filtration and cleaning of the vat, anodes, bags, connections and filters will generally be found beneficial where the properties of the deposit are below standard.

Permanganate Treatment for Re-conditioning Nickel Solutions Contaminated by Organic Impurities

The treatment should be carried out in a lead-lined tank from which anodes and all organic matter (*e.g.*, anode bags) have been removed.

The acidity of the solution is first increased if necessary to about pH 3 by the addition of sulphuric acid. Sufficient potassium permanganate (dissolved in water) is then added to produce a purple colouration which remains for 48 hours with the temperature of the solution maintained at about 35° C. 0·25 g. per litre or 2·5 lb. per 1,000 gallons, is usually sufficient and is recommended for new and for slightly contaminated solutions. If severe contamination is suspected a larger quantity of permanganate may be necessary ; the quantity required may be determined by the method indicated below. After standing for 48 hours, the residual permanganate is removed by the cautious addition, with vigorous stirring, of hydrogen peroxide. The solution is then filtered to remove precipitated manganese dioxide. This may be done conveniently by stirring finely divided kieselguhr into the solution (10–50 lb. per 1,000 gallons) and then filtering, preferably through glass wool. The acidity of the No. 1 (" Hard ") solution is restored to the normal (pH 5·5–5·9) by adding ammonia cautiously with vigorous stirring.

The quantity of permanganate required may be determined by treating a series of 100 c.c. samples of the solution, the acidity of which has been reduced to about pH 3·0, with increasing amounts of a 1 per cent. solution of potassium permanganate, *e.g.* (1) 2·5 c.c. ; (2) 5·0 c.c. ; (3) 7·5 c.c., etc. The samples, contained in flasks, are maintained at about 35° C. for 48 hours, for example, by suspending them in the nickel bath. The amount of permanganate to be added to the bulk solution is given by the minimum concentration required to maintain a purple colour. Thus, if all samples containing 5 c.c. or more are purple, 0·5 g. per litre (5 lb. per 1,000 gallons) of permanganate are required for treating the bulk.

If means for rapidly heating the solution are available, the time of treatment may be reduced to a few hours. The solution is heated to 80–100° C., and sufficient potassium permanganate solution is added to give a pink colour which should remain for 15 minutes ; if the pink colour disappears in less than 15 minutes, more permanganate solution should be added, but excess should be avoided. The solution should be allowed to stand for about one hour and if still pink, hydrogen peroxide should be added slowly and with vigorous stirring of the solution ; care should be taken to avoid adding more than is necessary to destroy the pink colour. The solution should then be filtered as soon as possible, kieselguhr being added to facilitate filtering (*see* above). It is not advisable to allow the solution to stand over night after the pink colour has disappeared, or has been destroyed by hydrogen peroxide, before filtering.

APPENDIX III

Stripping of Defective Nickel Deposits

Where removal of a defective deposit is necessary, choice must be made between a mechanical and an electro-chemical method. Mechanical methods, *e.g.*, machining are usually only economical on relatively simple contours and then generally involve the risk of removing steel and thus increasing the amount of repair required. On more elaborate repairs this method becomes difficult and costly. Unless a mechanical method has removed all traces of deposit, a final electro-chemical stripping should be carried out.

Electro-chemical stripping methods are somewhat critical in operation, lengthy in time and offer the risk of irreparable damage to the article by corrosion or anodic attack. The following method, if carried out exactly as described, is usually successful :—

> The article is de-greased, dried and hung, dry, in a sulphuric acid stripping tank containing a 50 per cent. solution of sulphuric acid by volume (65 per cent. by weight, sp. gr. 1·55). It is made anode, using lead cathodes and is connected through an ammeter direct to a 2-volt cell from a stand-by accumulator block. The nickel gradually dissolves, steel being unattacked. Complete removal of the deposit is shown by cessation of the current and a longer time is usually required than that used for deposition. On completion of the stripping the article is washed and dried and may then be re-treated. On no account should this operation be attempted using the low voltage mains current without seeking expert advice.

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