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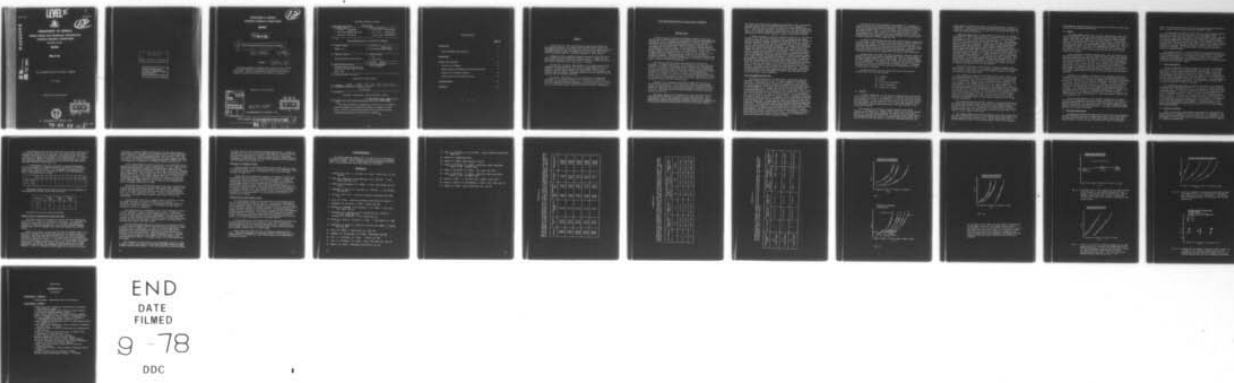
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MATERIALS RESEARCH LABORATORIES**

MELBOURNE, VICTORIA

REPORT

MRL-R-709

THE ELECTRODEPOSITION OF HIGH-PURITY CHROMIUM

L.H. Esmore

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ABSTRACT

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The electro-winning of chromium with a purity of up to 99.99% is described together with significant features of design of a pilot plant. Control of variables and their effects on electro-winning efficiency and quality of the product are reported.

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SUMMARY

A pilot plant for the electro-winning of high-purity chromium has been described earlier. The present paper provides further details and developments together with the results of several years of operation during which more than two tonnes of chromium with a purity often better than 99.99% (including oxygen but excluding hydrogen) has been produced.

Hydrogen was not an important impurity because the metal was melted under vacuum in the associated alloy research project. Oxygen was the major impurity because it remains as oxide inclusions in ingots and alloys and the aim, therefore, was to keep this to a minimum.

The influence of each process variable on the oxygen content of the chromium has been established. The electrolyte temperature was the most important, followed by the chromic acid and sulphate contents of the solution. Current density affects the oxygen content of the metal but the current values were always a compromise related to the run duration and the cathodic (electro-winning) efficiency.

The chromic acid/sulphate ratio in the electrolyte is generally considered to be a control variable in the deposition of chromium for decorative and engineering applications. In the present work, it is shown that each component functions independently, and that large changes in the ratio of the two have little effect on either the process or the product.

THE ELECTRODEPOSITION OF HIGH-PURITY CHROMIUM

INTRODUCTION

A regular supply of chromium of the highest possible purity was required for a research project on chromium-base alloys for high-temperature applications (1-5). Although electro-winning of chromium from trivalent electrolytes had previously been developed, and has a high cathodic efficiency, the metal obtained is impure and generally suitable only for the manufacture of ferrous alloys. On the other hand, chromium deposited from hexavalent chromic acid baths is intrinsically pure because few foreign metals co-deposit even when present in the electrolyte. Further, the foreign metals are generally present as cations and can be removed by ion-exchange techniques. Therefore, when the purity of the chromium is a paramount requirement, the disadvantages of the six-electron reduction from chromic acid and the well-known low efficiency of the process become tolerable, at least in a small-scale operation.

The sulphate-catalysed process was employed in the work to be described. To minimise impurities in the electrolyte, the whole bath was periodically treated by ion exchange and all added chromic acid similarly purified. This ensured freedom from traces of metals in the chromium and the remaining impurities were the non-metals hydrogen, oxygen and nitrogen. Hydrogen in the deposits varied in the range of 165-2,200 ml/100 g (0.015-0.2% by weight) but, because the metal was subsequently melted in a vacuum, this was easily removed. There are, however, some aspects relating to the nature of the hydrogen which are of more than academic interest and which will be dealt with in a further paper.

Nitrogen in the chromium has been shown by Ryan (6) to be due to nitrate in the electrolyte. It was found that analytical reagent-grade chromium trioxide from one source contained 60 ppm of nitrogen as nitrate, whereas the commercial electroplating-grade material contained less than 1 ppm (7). The latter material was used throughout the project after ion-exchange purification.

The oxygen content of the chromium was of major importance because oxide remains as inclusions in ingots and alloys after melting. In a comprehensive study of the influence of plating variables on the diverse properties of chromium deposited from sulphate-catalysed baths, Brenner et al. (8) determined the oxygen and hydrogen contents of the various deposits.

They found that, when the bath temperature was raised to 85°C, the deposits contained between 0.031 and 0.082 wt% oxygen which is a considerable decrease from the value of around 0.5% typical of bright deposits plated at 50°C. This trend was confirmed by Greenaway et al. (9), who confined their studies to the narrow temperature range of 72-87°C and produced chromium containing as little as 0.01% oxygen at cathodic efficiencies around 5%.

A similar programme of tests was conducted by Block et al. (10) and by Ferrante et al. (11) at the US Bureau of Mines, yielding similar oxygen contents at similar cathodic efficiencies and demonstrating that the loss of tree-like growths of chromium (dendrites) during deposition, was a major problem. The latter project was not a detailed study of process variables and the control devices used were elementary. For example, the electrolyte temperatures varied between 85°C and boiling point. These workers were, however, the first to use aluminium cathodes with squares scored in the surface to facilitate the removal of the chromium. They also experimented with ion-exchange purification of the electrolyte and confirmed the high cathodic efficiencies of fluoride-catalysed baths reported earlier by Ryan (12). These fluoride-containing baths operate at boiling point, adding to the problems of plant construction, maintenance and control. Brandes and Whittaker (13) experimented with various tank linings and anodes for the baths and finally chose polytetrafluorethylene (PTFE) beakers and palladium anodes coated with lead dioxide in an electrolyte saturated with lead chromate. The change in anode overcame the characteristic drop in cathodic efficiency observed by Ryan (12) and by Dale and Esmore (14). The metal produced contained 0.01-0.04% oxygen and, despite the higher efficiencies, the difficulties of plant maintenance prevented long-term operation and studies of process control parameters.

Plant Development and Operation

Concurrently with much of the above work, a pilot-scale plant was developed at these Laboratories for the regular production of kilogram quantities of chromium with as high a purity as possible. Safety devices and controls were incorporated to permit unattended continuous operation (including weekends). This plant has been described in considerable detail by Dale and Esmore (15). Sulphate was used as the catalyst because the operating temperature of the bath could be 85°C or even lower. This reduced the problems with materials of construction and, because the tank top was open, the installation of control devices was easier. As the influence of each process variable was assessed, control devices were improved to maintain the required degree of control. An automatic current controller was devised by Esmore (16) to stabilise the rectifier output to within 1% of the usual 1000 A operating level. Coupled heating using silica-sheathed heaters, and cooling by a tantalum coil with mains water, maintained the bath temperature within 0.5°C. The electrolyte level was maintained to better than 1 mm by a distilled water supply and a float-operated valve with ball-bearing pivots. Spray losses in the exhaust gases were controlled by a rigid PVC cover incorporating a series of concentric baffles and supported on a titanium frame about 100 mm above the electrolyte level. This minimised the loss of water, chromic acid and sulphate and thus assisted in the maintenance of electrolyte composition as well as plant efficiency.

The chromic acid was replenished by the addition of a solution at a concentration of 100 g/l which had been established to be a satisfactory level for efficient ion-exchange purification. This was fed by a PVC disc and bucket reagent feeder at a pre-determined rate to maintain the bath concentration at all times within 5 g/l of the required level or better. The sulphate level in the electrolyte was maintained within 0.1 g/l by the amount present as an impurity in the regular additions of chromic acid and by small quantities of dilute sulphuric acid.

A series of safety devices was installed to guard against leakage from the tank, high or low electrolyte levels, and failure of either the exhaust system or power supply. The probes on the electrolyte level devices originally were platinum but these were found to corrode in the electrolyte after long service and so were replaced by titanium rods. All devices were fail-safe in their design and their reliability enabled continuous unattended operation for the long periods necessary to study the process.

During several years more than 1500 experimental runs were carried out producing more than two tonnes of chromium with a purity often exceeding 99.99%, including oxygen but excluding hydrogen. When the demand exceeded the 1000 A capacity of the plant, a 4000 A plant was constructed at Ordnance Factory, Maribyrnong. This operated as a production unit supplying local requirements and those of research teams in England and USA. It released the pilot plant from its dual role and allowed investigations to be made in wider areas of interest.

Details essential to the successful operation of the plant are discussed under the following headings :

- (a) Cathodes
- (b) Anodes
- (c) Electrolyte maintenance
- (d) Stress measurements
- (e) Analysis of chromium

(a) Cathodes

In earlier experiments, a steel shim was wrapped around a cylindrical former and held in place by a retaining key, as described previously (15,17). After plating, the stress in the deposit was not evident until the retaining key was released. If the stress was highly tensile, the shim would enlarge and could easily slide off the former. On the other hand, when the stress was compressive, the shim adhered strongly to the former and had to be broken off in pieces.

The introduction of aluminium cathodes presented new problems. Firstly, if the deposit had a highly tensile internal stress and the abraded surface was not sufficiently roughened, the deposit would crack during plating. If the crack was wide enough, the cathode would be lightly plated with chromium through the fissure. At somewhat lower stress values, the crack would allow the electrolyte to reach the aluminium surface but the

current would be insufficient either to plate the surface or to protect it cathodically. Under these conditions the aluminium corroded, generally at a weld area, with perforation of the 4-mm wall of the tube which caused the cathode to fill with electrolyte.

High compressive stress in the deposit made removal of the chromium very difficult. Under these conditions, the cathode surface did not require roughening; in fact, the smoother it was the better. The contractile characteristics of the deposit ensured adequate adhesion. This chromium had a very low oxygen content and, because the alloy project required major amounts of metal of this quality, a large number of production runs were conducted under these conditions. These deposits always spalled when removed from the plating tank and would often detach from the aluminium surface explosively when sprayed with cold water, embedding particles in the lead lining of the rinse tank. The metal also spalled violently when the remaining deposit was tapped with a hammer, making the task of removal of the metal a hazardous operation. A protective face shield and drop sheets were necessary to avoid injury to the operator and loss of chromium. This characteristic of low-oxygen chromium was observed by Brenner et al. (8) but the causes were not established. A further characteristic of this chromium is a peculiar oblique fracture mode and the complete absence of any visible crack pattern, even in thick deposits.

For most of the alloy research project, chromium containing about 0.01% oxygen was satisfactory. This could be deposited on smooth aluminium surfaces with a stress level that provided adequate adhesion yet allowed easy removal by light hammer blows.

The cathodes were fabricated from 6063 aluminium alloy tubing in the precipitation-hardened condition, and consisted of a length of the tubing with welded-in solid ends. The bottom end was turned to a hemisphere and the top consisted of a parallel portion tapering above the solution level to an integral screw-threaded section for the d.c. power connection. The wall thickness of the tubing was about 4 mm. The whole assembly was sufficiently resilient in the plated area to allow removal of the chromium by light hammer blows without deformation of the aluminium, thereby ensuring long service life. Variation of the current density was obtained by using three cathode diameters, namely, 50, 80 and 110 mm. The cathodes were masked with a heavy grade of PVC tape to give a plated length of 530 mm measured from the hemispherical tip. The 1000 A rectifier was always operated at its maximum output yielding current densities of 130, 75 and 55 A/dm² respectively.

The electrowinning efficiency was related to the anode configuration, the plated length of the cathode, the position of the hemispherical tip of the cathode with relation to the anodes, the current density, and the duration of each run. All of these factors contributed to the control of dendrite growth, which has been the major production problem noted in the reports of other workers in the field.

The normal schedule of operations consisted of two runs of about 51 h each plus a weekend run of 66 h. For the shorter runs, 80 mm cathodes were used but where the time extended to 66 h, 110 mm cathodes were used to minimise dendrite losses. A very limited number of runs of 24 h duration

were conducted with 50 mm cathodes but the reduced resilience of these made removal of the chromium more difficult.

(b) Anodes

The anode assembly consisted of a copper ring 300 mm dia. made from 50 mm x 6 mm busbar. This was fixed above the tank and supported 8 equispaced solid lead-alloy anodes each of 50 mm diameter and 740 mm overall length. These rods were easily cast and easily replaced. Flat surfaces were cast at the upper ends to ensure good contact with the copper ring to which they were bolted. The rods passed through a rigid PVC tank cover and terminated 75 mm above the level of the hemispherical cathode tip. They were masked with PVC tubing above the solution level and 75 mm below it. The effective length of each anode was thus 150 mm less than the plated length of the cathode.

In the interests of maximum chromium purity, pure lead anodes would have been preferred but it was found that even brief current interruptions resulted in passivity when they were used. Once the inert surface formed, the electrical resistance of the layer caused the plating tank voltage to rise from the normal 6 V to more than 15 V. Anodes in this condition have been observed with a red-hot surface, visible through the surface of the electrolyte; in such cases resulting in thermal run-away of the bath. Anodes cast from chemically pure lead with an addition of 0.2% tin overcame this problem. Even after protracted periods of idleness in the solution, these anodes showed complete recovery to the active state after one hour of operation.

Throughout the programme, variations in the trivalent-chromium concentration in the electrolyte were observed and, from graphical records of all factors involved in the process, it seemed that there may be a connection between this concentration, the cathodic efficiency, the oxygen content of the deposit, and the internal stress in the deposit. The actual concentration of the trivalent ion was plainly at an equilibrium level between its formation at the cathode and its re-oxidation to the hexavalent state at the anode. It is generally known that high concentrations of trivalent ion (and other cations) can cause a conventional plating bath to become inoperative due to low electrolyte conductivity. On the other hand, it is common practice to add reducing agent to a new plating bath to produce some of the trivalent ion.

A study of the influence of the trivalent chromium ion on cathodic reactions as an independent variable, however, requires that the anode area alone be changed while all other factors are held constant, and that all observations relate to the equilibrium state. The anode assembly described earlier, coupled with the precise controls in this plant, provided a unique opportunity to examine this aspect.

(c) Electrolyte Maintenance

Ion-exchange processes were employed to remove traces of foreign metals from the electrolyte and from all added chromic acid. On an annual basis, the whole bath was diluted to a concentration of about 100 g/l CrO_3 and passed through a column of Permutit "Zeo-Karb 225" resin in the hydrogen

form. All chromic acid added to the bath was first dissolved in distilled water to yield a 100 g/l concentration and similarly treated.

In operating the column, the fresh resin was in the hydrogen form but, after use, the beads were discoloured due to the exchanged cations. Regeneration of the resin was carried out with 10% sulphuric acid. When the resin was in contact with acids the bed contracted and it expanded again to its original volume after rinsing with water. After long use it appears that this caused bead fracture and this seems to be the major cause of resin deterioration. The broken beads packed more closely in the column causing a decrease in flow rate. Washing the column by reverse flow was used at intervals to segregate the fractured beads into the upper layers and to remove the finest particles.

As mentioned earlier, a locally-manufactured electroplating grade of chromium trioxide had a very low nitrate content essential for the production of low nitrogen chromium. It was dissolved in 20-kg batches, settled and treated by ion-exchange prior to feeding to the bath. The electrolyte composition was controlled by density measurements and by tri-weekly analyses of the CrO_3 , Cr^{3+} and SO_4^{--} levels.

(d) Stress Measurements

The use of aluminium cathodes was practical only when some knowledge of the stress levels in the chromium deposit was available. As will be shown later, the relationship between stress and the oxygen content made measurements of this property valuable for quality control of the metal. The measurements made were not absolute and, indeed, true determinations of internal stress in chromium deposits may be impractical. It is well known that the chromium plating bath has poor throwing power so that the deposit is not uniform in thickness, furthermore, it is known that the stress level varies as the deposit increases in thickness.

For comparative measurements, strips of shim steel 0.35 mm thick and 16 mm wide were masked with Sellotape No. 771 to expose a length of 100 mm on one side only. (Sellotape No. 771 is a polyester film, 25 μm thick with a synthetic adhesive. It was not affected by the bath at temperatures, even up to boiling point, during 2 h tests). The test strip was mounted in a shield to restrict the current at the edges and ends so aiming at uniform deposit thickness. The whole strip, 300 mm long overall, was gripped at one end allowing the plated area to bend freely during plating. The curvature of the strip after plating was determined in a jig consisting of a tool-maker's vice and micrometer-screw assembly. The mean thickness of the deposit was determined by dissolving the steel in nitric acid and weighing the residual chromium.

(e) Analysis of Chromium

Early in the project, polarographic techniques were investigated for determining metallic impurities in the chromium (18). An advantage of this method is that standardisation could be carried out by the addition of suitable amounts of a very dilute solution of the appropriate metallic impurity to a duplicate determination.

Samples of up to 5 g were dissolved in a mixture of hydrochloric and perchloric acids, the chromium volatilised as chromyl chloride and the copper, iron and lead impurities in the residual solution were determined from a single polarogram using a supporting electrolyte of alkaline triethanolamine. The use of acids purified by distillation and a purified supply of hydrochloric acid gas were essential to keep reagent blank corrections to a suitably low level. Similar preliminary steps were used with a supporting electrolyte of sulphuric acid for the determination of silver. The nature of the brown stains on the chromium and in the crack structure were also examined by treating the chromium sample briefly with concentrated hydrochloric acid. The resultant solution and the cleaned chromium were analysed separately for the trace metals - copper, lead and iron.

Spectrographic techniques were also developed (19) using similar techniques for the volatilisation of the chromium and using pure calcium carbonate as a matrix to convey the residual impurities to the arc of an emission spectrograph. Reagent impurities limited the reproducibility in this analysis to 1 ppm for Mg, Pb, Fe, Cu and Ag and to 2 ppm for Al.

Samples of some batches of the chromium were also analysed by mass spectrometry at the National Physical Laboratory, Teddington, Middlesex, U.K.

The determination of hydrogen, oxygen and nitrogen in the chromium was the subject of considerable study (20,21). Because of the large number of determinations required in the project, a new high-capacity vacuum-fusion unit was devised (22), and later modified to include gas chromatography. For the very large number of oxygen determinations required, the Adcock (23) method was first employed. This was improved and finally compared with vacuum-fusion techniques (24). The improvements resulted in the rejection of a very large number of early results and the repetition of experiments in specific areas. The significance of oxygen as an impurity has already been stated to be a major consideration in the work.

EXPERIMENTAL

As a general rule, the composition of the electrolyte was held constant for a period and a series of tests conducted at 5°C temperature intervals. Sufficient runs were conducted at each temperature to evaluate the reproducibility of the oxygen content of the chromium, the cathodic efficiency and the internal stress in the deposit. Considerable effort was expended on studies of the inter-relationship between the current, cathodic (electrowinning) efficiency and the oxygen content of the product metal. The growth of chromium dendrites on a cathode is undesirable because they break off and fall to the bottom of the tank. Although this metal can be recovered, it is contaminated with lead-chromate sludge and has to be regarded as lost production. Other workers in the field (9,10,11,12) were able to achieve only about half the efficiencies obtained in the present work for this reason. The compromise between current density and run duration, previously mentioned, was based on observations of dendrite growth. A closer study of the influence of current density was conducted using three

cathode diameters with identical masked lengths to give nominal current densities of 55, 75 and 130 A/dm². (The current densities were calculated on initial cathode dimensions assuming a smooth surface even though light grit blasting was used at times.) The durations for each experiment were calculated to give the same ampere-hours per square decimetre. Throughout the series of tests, the bath composition and temperature were held constant and at least four runs were conducted with each cathode and the results averaged.

To isolate run duration as a single variable, a series of experiments was carried out where the cathode dimensions, bath composition and temperature were held constant. Durations of 25, 50, 66 and 90 h were employed for a replicate series and the results averaged.

The concentrations of the two bath constituents, chromic acid and sulphate, were varied over a wide range at each temperature and the oxygen contents in the resultant chromium were recorded. The influence of the trivalent chromium concentration in the electrolyte was studied by progressively reducing the number of anodes from the normal eight to four, then to three, and operating for several test runs in each instance.

RESULTS AND DISCUSSION

Purity of the Chromium

A major finding from the polarographic analyses concerned the significance of the brown stains on inadequately-rinsed deposits. When a 10 g sample of this metal was briefly treated with re-distilled hydrochloric acid, the stains were rapidly dissolved with a weight loss of only 13 mg. The resultant acid solution and the cleaned metal were separately analysed polarographically for Cu, Pb and Fe with the following results :

Impurity	In Surface Stain, μg	In Clean Chromium, μg	Total Impurity ppm	Impurity in Surface Stains %
Cu	4.7	4.5	0.9	51
Pb	10.4	9.3	2.0	53
Fe	21.5	7.6	2.9	74

The stains are apparently formed by the reduction of the chromic-acid electrolyte by the chromium metal when the solution is allowed to dry on the surface. (The above analyses were carried out early in the programme and prior to the introduction of ion-exchange treatments). The stain, therefore, may be taken to be hydrated chromic oxide containing impurities present in the electrolyte.

The recognition that this was a major source of metallic impurities in the chromium, coupled with the fact that, after heating, the stain became anhydrous chromic oxide and contributed to the oxygen content of alloys, resulted in the regular post-treatment of all metal produced. For chromium from shim steel cathodes, a hydrochloric acid treatment was used. Later, when aluminium cathodes were adopted, the metal was treated with sodium hydroxide followed by hydrochloric acid.

A vacuum-degassed composite 2 kg parcel of chromium from Runs No. 730-733 was supplied to the National Physical Laboratory for inclusion in their stock of very pure metals. This consignment was analysed by the emission spectrograph at our laboratories and by a mass spectrograph at N.P.L. The results were as follows :

	Mn	Pb	Cu	Ag	Fe	Sn	V	As	P	Ni	Si	Mg
M.R.L. ppm	2	6	1	3	5	-	-	-	-	1	1	2
N.P.L. ppm	3	7	1	4	5	4	3	1	1	1	-	-

The gaseous elements were determined by vacuum fusion techniques at both laboratories and the results were as follows :

Laboratory	Oxygen ppm	Nitrogen ppm	Hydrogen ppm
M.R.L.	51	5	-
N.P.L.	50	6.5	0.2

This metal has a purity better than 99.99%.

Oxygen Content of Chromium and Cathodic Efficiency

The oxygen content of the metal was not only the major impurity but, in addition, it formed oxide inclusions in the alloys. It is possible to reduce the oxygen content of chromium by a protracted high-temperature treatment in a hydrogen atmosphere but, for the alloy research programme, adequate metal with an acceptably low content was produced for critical studies.

Early in the project, it was found (15) that the oxygen content of the deposit was related to the cathodic efficiency and the internal stress in the metal. The present work has established that, at a given electrolyte temperature within the range 81-91°C, the oxygen content is controlled by the solution composition. Figs. I, II and III contain contours drawn through points of equal oxygen content and show that, over a wide range of solution compositions, the current efficiencies and oxygen contents do not change appreciably, provided that the temperature and current density are held constant. In Fig. II, taking the 0.005% oxygen line, the ratio of chromic

acid (CrO_3) to sulphate ($\text{SO}_4^{=}$) varied between 37 and 82 without change in oxygen content and, furthermore, the efficiency did not change appreciably. This is contrary to commonly accepted opinion that the ratio, $\text{CrO}_3 : \text{SO}_4^{=}$, is a control variable in chromium deposition. The three figures also show that there is no condition over the range studied where chromium containing 0.01% oxygen can be deposited at efficiencies greater than about 8%.

Only a limited amount of work was carried out at 76 and 96°C and the results are shown in Figs. IV and V, respectively. At 76°C, bright chromium deposits were obtained at chromic-acid concentrations between 370 and 410 g/l with oxygen contents between 0.02 and 0.03%. Under these conditions, the cathodic efficiencies were between 4 and 7%, which is much lower than at higher temperatures. These deposits were not unlike conventional decorative deposits but the latter have oxygen contents above 0.5%. At 330 g/l CrO_3 the deposits changed to a dull matte texture with cathodic efficiencies around 8-10% and oxygen contents of 0.02-0.03%. These observations have little commercial significance but they do indicate that chromium with a fairly low oxygen content can be bright.

The difficulties of operating the plant at 96°C were considerable due to the high water consumption, the additional heating power required, and problems with materials of construction. The work at this temperature aimed at the high efficiencies found by Ryan (12) in fluoride-catalysed baths, but no such conditions were found. The major observation was that the sulphate concentration had a smaller effect than it did at lower temperatures.

A group of four curves for an oxygen content of 0.02% Fig. VI shows the marked influence of the three variables so far discussed. In particular, they show the effect of bath temperature and why the present studies have achieved a reproducibility not achieved by others where temperature control was inadequate.

The reproducibility of experimental runs is also indicated in Table 1, in which results for randomly selected weeks are shown. As mentioned earlier, each week covered two runs of approximately 50 h and one of about 65 h with current densities adjusted appropriately. The table shows the constancy of bath composition, efficiencies and oxygen contents during each week and the effect of the change in current density. The conditions of operation were changed from week to week.

The inter-relationship between the duration of a run and the current density on both the oxygen content of the metal and the efficiency is shown in Tables 2 and 3, respectively. In Table 2, the bath compositions, temperature and current density were maintained constant and only the durations of the runs were varied. Replicate tests were carried out for durations of 25, 50 and 66 h with a single experiment at 90 h. Although 25 h runs were more efficient, the removal of the thin deposits from cathodes was more difficult. The oxygen content of the thin deposits was also higher.

The influence of current density as an independent variable is shown in Table 3, which lists results for runs where the ampere hours per square decimetre had been held constant. The current density was varied by change

of cathode size and the run duration adjusted appropriately. Although the variation in current efficiency was not large under the varying conditions, some advantage is evident at the lowest current density. The oxygen contents of the deposits were markedly affected, with the highest values at the highest current densities. The two tables demonstrate the precision in control achieved, and the need for it.

Influence of Trivalent Chromium

When the number of anodes was reduced from the normal eight to three, the equilibrium level of the trivalent ion doubled but no appreciable change in either the oxygen content of the deposit or the cathode efficiency resulted (see Fig. VII).

These results are interesting, because it is generally accepted that the trivalent ion is involved in the cathode film formation on which the six-electron reduction of chromic acid to metal depends. It should be realised that the concentration of the ion in the electrolyte, determined in the present study, is at an equilibrium level arising from two simultaneous reactions, namely, that at the cathode where large amounts of the ion are produced and that at the anodes where an almost equal amount is re-oxidised to chromic acid. What remains in the body of the electrolyte is related to the rate of formation at the cathode, the agitation of the solution due to gases generated at all electrodes and the rate of re-oxidation at the anodes.

Internal Stress versus Oxygen Content

The relationship between the internal stress in the chromium deposit and the oxygen content is shown in Fig. VIII, the broad band depicting the scatter in observed values in many hundreds of experiments. The variations are not unexpected because the residual stresses in any situation are related to the well-known cracking of chromium deposits. It has been proposed by Snavely (25) that chromium is deposited as a hydride and that this decomposes during the deposition process. The resultant shrinkage produces triaxial stresses which, in a relatively thin brittle metal, produce a network of cracks. The penetration of electrolyte into the voids produced by cracking results in the oxide contamination of the chromium deposit.

In the present work, the chromium which was compressively stressed had a high hydrogen content and was crack-free (a term used in decorative chromium practice) even at a thickness exceeding 1 mm. Such metal always had an oxygen content below 0.01% whereas metal showing tensile stress had lower hydrogen contents and up to 0.05% oxygen.

These observations indicate that the mechanism proposed above is valid. During the programme, a considerable amount of additional data was accumulated which confirms this, and a further paper will be published on this specific aspect.

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T A B L E 1

Typical records for the production runs at 86°C, showing the reproducibility of bath conditions and the resultant oxygen contents of the chromium and the cathodic efficiencies. The third run in each bracket also shows the effect of the long week-end runs at lower current density.

Run No.	Duration h	Current Density A/dm ²	Bath Composition CrO ₃ SO ₄ g/l g/l		Cath. Eff. %	Oxygen Content %
955	51.0	75	224	3.21	9.3	0.018
956	51.6	75	226	3.23	9.5	0.014
957	65.6	55	229	3.23	8.6	0.012
973	50.2	75	223	3.82	10.4	0.027
974	51.6	75	223	3.84	10.4	0.023
975	65.3	55	226	3.85	10.6	0.018
1074	51.9	75	238	5.98	10.1	0.055
1075	51.6	75	237	5.93	9.9	0.055
1076	65.3	55	239	5.93	10.1	0.046
1141	47.4	75	273	7.14	10.3	0.036
1142	51.7	75	272	7.13	10.1	0.033
1143	65.3	55	268	7.10	8.8	0.027
1302	50.4	75	263	4.04	8.0	0.005
1303	51.3	75	266	4.14	7.7	0.006
1304	65.7	55	265	4.16	7.1	0.004

T A B L E 2

A replicate series of experiments showing the effect of run duration on the cathodic efficiency with constant bath composition, current density (75 A/dm²) and temperature (86°C). The oxygen contents of deposits from 25 h runs are a little higher than for runs of 50 h and longer.

No. of Runs	Run Duration (mean, h)	Current Effic. (mean, %)	Electrolyte Composition		Oxygen Content (mean, %)
			CrO ₃ (mean, g/l)	SO ₄ (mean, g/l)	
1	90.2	7.2	287	6.05	0.012
7	66.3 ± 0.5	8.5 ± 0.3	287 ± 2	6.01 ± 0.05	0.013 ± 0.001
14	50.9 ± 0.3	9.1 ± 0.2	285 ± 1	6.03 ± 0.06	0.013 ± 0.002
16	25.0 ± 0.2	10.2 ± 0.1	285 ± 2	5.99 ± 0.06	0.018 ± 0.002

T A B L E 3

A replicate series of experiments showing the influence of current density on the oxygen content of the chromium and the cathodic efficiency when the coulombs per unit area, bath composition and temperature (86°C) are held constant.

Current Density A/dm ²	No. of Runs	Run Duration (mean, h)	Current Effic. (mean, %)	Electrolyte Composition CrO ₃ (mean, g/l)	SO ₄ (mean, g/l)	Oxygen Content (mean, %)
130 (= 3263 Ah/dm ²)	5	25.1 ± 0.6	9.1 ± 0.1	284 ± 4	5.89 ± 0.06	0.021 ± 0.003
75 (= 3795 Ah/dm ²)	5	50.6 ± 0.6	9.1 ± 0.2	284 ± 1	5.99 ± 0.08	0.014 ± 0.002
55 (= 3652 Ah/dm ²)	4	66.4 ± 0.5	9.7 ± 0.1	281 ± 4	5.94 ± 0.05	0.011 ± 0.001

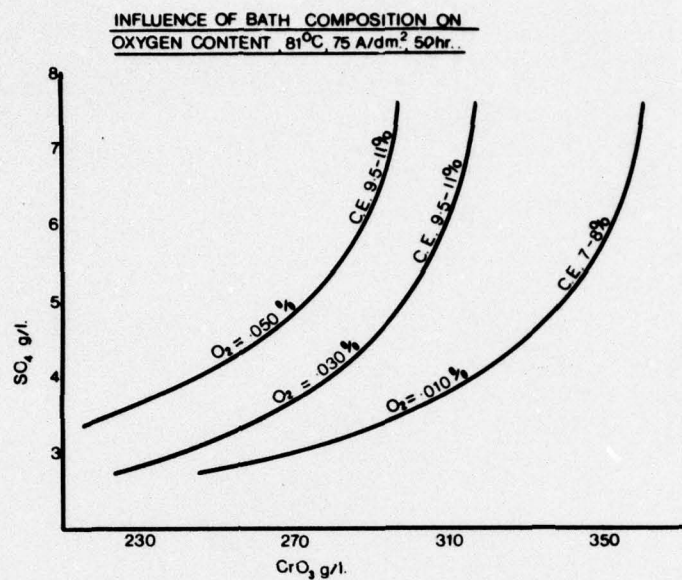


FIG. I

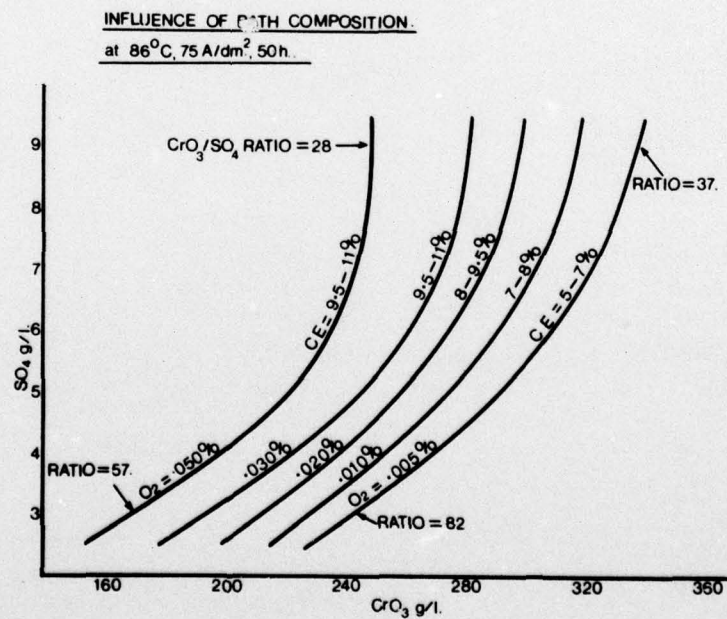


FIG. II

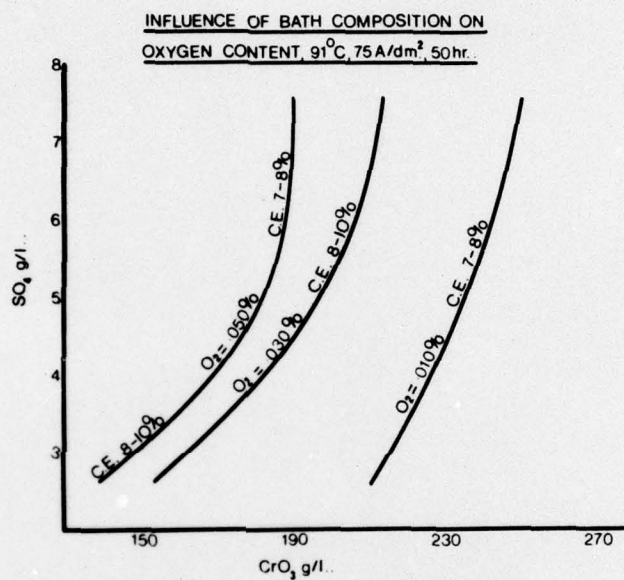


FIG. III

The influence of the chromic acid and sulphate concentrations on the oxygen contents of the chromium and the cathodic efficiencies (C.E.) at 81, 86 and 91°C, respectively. Fig. II also shows that the CrO_3/SO_4 ratio is not a control variable. All curves are contours for conditions yielding the same oxygen contents from several hundreds of experiments in which the current densities and run durations were practically constant.

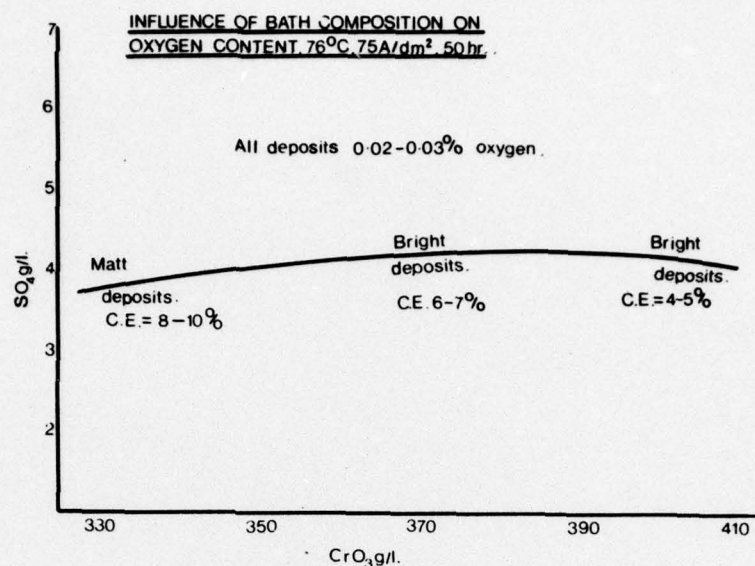


FIG. IV - Production runs at 76°C showing that the oxygen contents of the deposits are not markedly affected by large changes in the chromic acid concentration but that the deposits change from bright to matte in appearance. The curve is a contour for conditions yielding the same oxygen content.

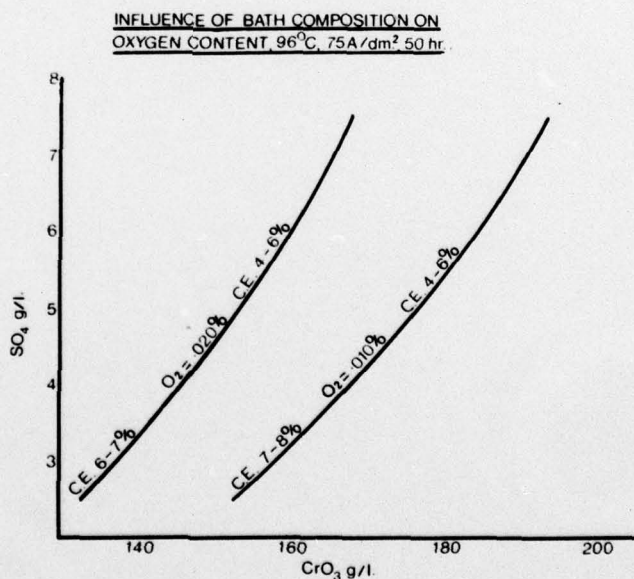


FIG. V - Contours for conditions yielding chromium with the same oxygen contents at a constant bath temperature of 96°C. The sulphate content of the bath has less effect than at the lower temperatures studied and the cathodic efficiencies are also lower. The scale for the CrO₃ ordinate differs from that in Figs. I - III.

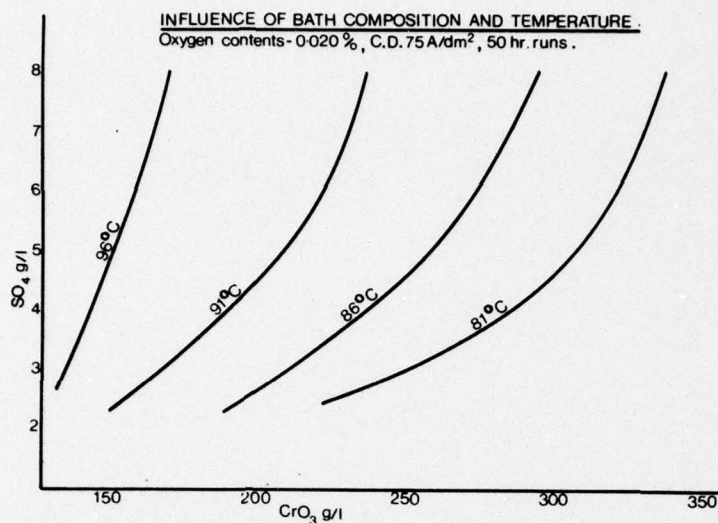


FIG. VI - A series of contours for conditions which yield chromium with oxygen contents of 0.02% showing the influence of bath temperature and bath compositions. This grouping shows the changing slopes of the contours for the four temperatures.

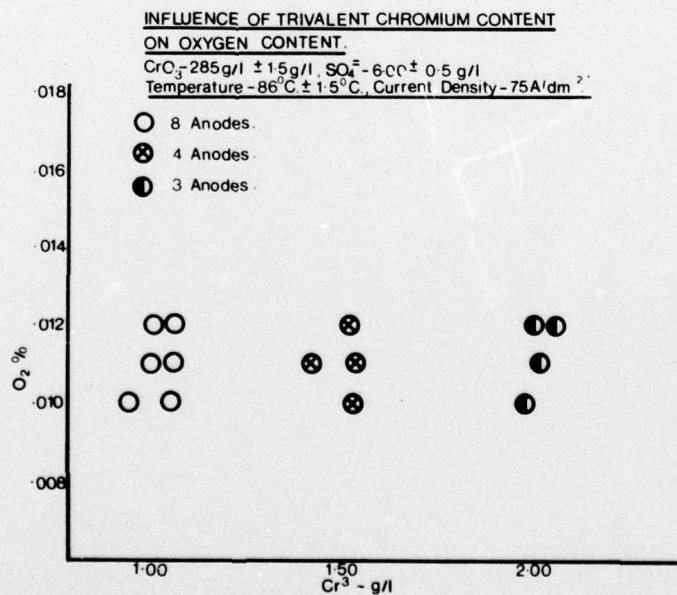


FIG. VII - Showing that the change of anode area, which results in a change in the trivalent-chromium content of the electrolyte, does not affect the oxygen content of the chromium deposit when all other variables are constant.

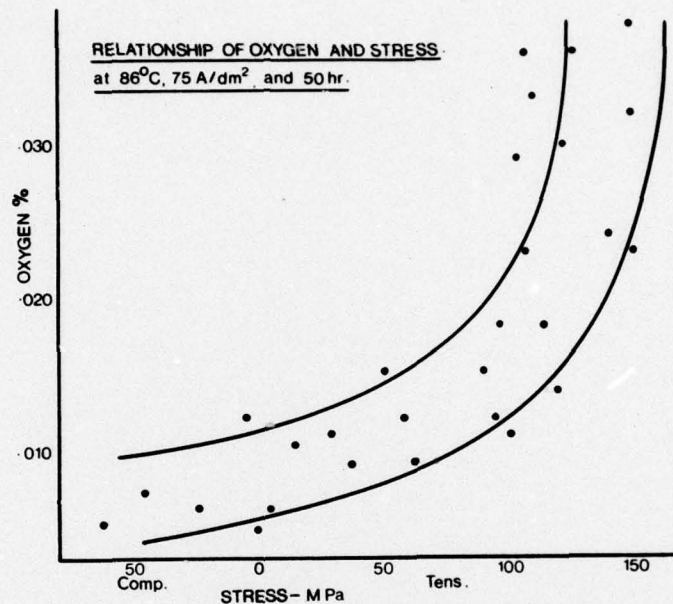


FIG. VIII - The broad band encompasses a range of results showing the relationship between oxygen contents of the chromium deposits and the internal stress. The changes were achieved by changing the bath compositions at constant temperature (86°C), current density (75 A/dm²) and with run durations of about 50 h. The figure represents several hundreds of production runs where stress measurements were carried out daily.

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